This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

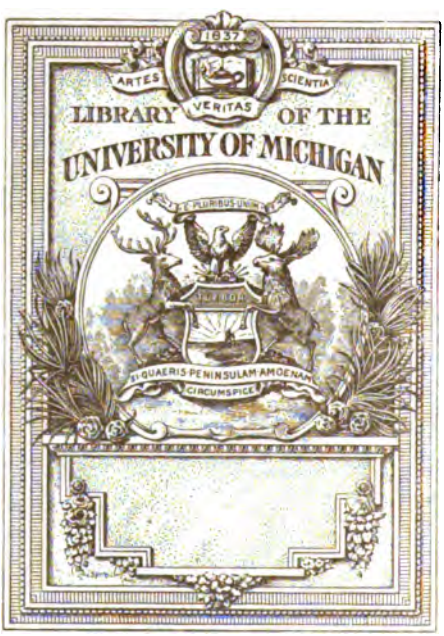
+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

B 466040


1837
ARTES
VERITAS
SCIENTIA
LIBRARY OF THE
UNIVERSITY OF MICHIGAN
E PLURIBUS UNUM
SI QUAERIS PENINSULAM AMOENAM
CIRCUMSPICE

East Engin.
Library
TP
145
.W2.4t

(PAUL SCHUETZENBERGER)

TECHNOLOGY OF CELLULOSE ESTERS

A THEORETICAL AND PRACTICAL TREATISE ON THE ORIGIN, HISTORY, CHEMISTRY, MANUFACTURE, TECHNICAL APPLICATION AND ANALYSIS OF THE PRODUCTS OF ACYLATION AND ALKYLATION OF NORMAL AND MODIFIED CELLULOSE

INCLUDING

NITROCELLULOSE, CELLULOID, PYROXYLIN, COLLODION, CELLOIDIN, GUNCOTTON, ACETYLCELLULOSE AND VISCOSE, AS APPLIED TO TECHNOLOGY, PHARMACY, MICROSCOPY, MEDICINE, PHOTOGRAPHY AND THE WARLIKE AND PEACEFUL ARTS

BY

EDWARD CHAUNCEY WORDEN, Ph.C., B.S., M.A., F.C.S.

AUTHOR "NITROCELLULOSE INDUSTRY"

In Ten Volumes

VOLUME EIGHT

Carbohydrate Carboxylates

(Cellulose Acetate)

ILLUSTRATED

NEW YORK

D. VAN NOSTRAND COMPANY

25 PARK PLACE

1916

Copyright, 1916

by

EDWARD CHAUNCEY WORDEN

Rose Press, Inc.
Newark, New Jersey

To

My First Instructor in Chemistry

Professor De Forrest Ross

Then and now, Professor of Natural Sciences, Ypsilanti (Mich.)
High School

This Work, in Grateful Appreciation

is

Affectionately Dedicated

The difficulties and discouragements of "research" exceed those of any other calling or any other occupation. Obstacles within the subject itself are immeasurable, indefinite and inexorable. Obstacles without are dispiriting and distracting. The research man regardless of his associates is a solitary soul without an effective sympathy from his associates in his intellectual campaign. He is surrounded as a rule with a spirit of conservative pessimism and supercilious doubt. Even his own mental integrity and sanity is apt to be questioned.

ANNOUNCEMENT.

All efforts of attempted merit have an aim. The aim of this work, the "Technology of Cellulose Esters," is to present the entire subject of the combinations of normal and modified cellulose with acid radicals in such completeness, accuracy and detail, that inability to find in the Collective Indices the information desired, will be trustworthy evidence that the matter sought was either ephemeral, irrelevant, inaccurate, valueless or non-existant.

For convenience in obtaining and handling, the subject matter will be divided into ten approximately equal volumes, paged consecutively and obtainable separately. Each part will contain full indices, the Patent, Name and Subject Index of the entire work being embodied in Volume Ten. This index will comprise over 40,000 patent citations, an enumeration of the work of 11,000 different investigators, and a Subject Index of upwards of 52,000 entries, the data for the completed work having now been collected and systematized. The illustrations exceed 600. Volumes One and Two are in the press; Volume Three nearly ready, the intention being to issue the remaining volumes at frequent intervals.

The general scope of the entire work is as follows: Vol. I will contain full information concerning normal and modified cellulose, the hydro- and hydral-celluloses, oxycellulose, and the chemistry and application of normal and hydrolyzed cellulose and starch. The history, chemistry and preparation of cotton for esterification, from the original bale of untreated cotton to the production in condition suitable for nitration; and the history, properties, manufacture and chemical and ballistic tests for the various forms of nitrated carbohydrates, including manufacturing details, specifications, scale drawings and photographs complete this part.

The cellulose esters have comparatively few uses in the dry state, exhibiting their usefulness more forcibly when in solution, either in the fluid or plastic state. Volume II enumerates the cellulose ester solvents, including fusel oil, and the amyl alcohols, amyl acetate and homologous esters, natural and synthetic camphor, and the large number of plastic-inducing bodies which have been proposed from time to time as substitutes for, or adjuncts to natural camphor. These solvents are extensively employed in the formation of paint and varnish solvents and finish removers, and in the preparation of substitutes for spirits of turpentine.

Vol. III comprises an enumeration of the various mechanical appliances for transforming the raw cellulose esters into finished products for use in the arts, with the types of machinery best adapted thereto. The preparation and uses of the fluid pyroxylin preparations, lacquers, bronzing liquids, enamels, impregnating media and waterproofing of textiles, the formation of artificial and imitation leathers, and the coating of skins and hides with cellulose ester solutions are illustrated and described.

290819

Those solutions which, when projected through capillary orifices into coagulating or hardening media, result in the formation of artificial silk and other filaments, broadly comprise the subject matter of Volume IV.

The entire subject of the history, chemistry, development and ramification of the pyroxylin plastic industries typified by celluloid and the various analogous products and substitutes therefor, constitute Vol. V.

The multiplicity of uses to which collodion and other nitrated celluloses have been applied in photography, medicine, surgery and pharmacy, including the industry of continuous film formation, are involved in Vol. VI.

Vol. VII constitutes the higher cellulose nitrates, gun cotton, the manufacture, applications and composition of the various smokeless powders, gelatins and nitrocellulose explosive combinations, including the applications of colloidin and the lower cellulose nitrates to microscopy, biology and bacteriology.

In the 530 pages involving Volume VIII are enumerated the water-insoluble carbohydrate carboxylates, specifically the cellulose acetates and formates and other uninflammable cellulose esters, including the entire sphere of formation, solvents, industrial applications and analysis. The indices to this volume contain 7,500 citations.

The cellulose sulfocarbonates, viscose, viscoid and similar bodies, with their methods of manufacture, differentiation and technical usefulness are elaborated in Vol. IX, while the final volume (X) contains a resume of the methods which have been proposed from time to time for the safeguarding of this art ,the safe transportation and handling of the products and the collective indices of the previous volumes.

A serious and ever growing problem in connection with a work of this breadth has been to restrain its size, and yet correlate and analyze the prodigiously prolific literature accumulated during the past seventy years. By a judicious selection of the more important and general observations for insertion as the text portion (ten point type), reserving the detailed, more abstruse and intricate parts for insertion in the foot-notes (eight point), it is planned to properly encompass the entire subject matter—equivalent in extent to about 9,500 octavo pages of ten point reading matter, into ten volumes of 400-600 pages each. To economize space, therefore, the notes in fine print may occupy the major portion of the work. No attempt will be made to curtail or reduce the number or completeness of the bibliographic references, which will exceed 90,000. The work issues in a limited edition from linotype composition, which is being dismantled after the printing of each folio.

Millburn, New Jersey, May 13, 1915.

PREFACE TO VOLUME EIGHT.

THIS portion of "Technology of Cellulose Esters" attempts to adequately cover the entire field of the water-insoluble Carbohydrate Carboxylates—specifically the Cellulose Acetates and Formates—whose claim to industrial recognition is characterized by their low burning capacity, in distinction to the corresponding nitric esters whch are both inflammable, combustible and explosive, and in contradistinction to the pyroxylin plastics typified by celluloid, which exhibit a well marked thermoplasticity at temperatures below that of boiling water.

The theoretical aspect of the subject is complicated by the phenomena of partial hydration coincident with and subsequent to esterification, which finds no analogue with the similar nitric esters—and in which whole series of analytically indistinguishable products undoubtedly arise from the progressive withdrawal of acid content from the acidyl-cellulose.

The technical applications proposed for these esters, in general, cover the ramifications of the entire field of the older, more widely developed and highly specialized nitrocellulose industry. The unusual activity of this art at the present day renders impossible its tratment in the perspective of elapsed time.

The fact that no work in any language exists on this subject at present—the voluminous available information being widely scattered throughout more or less abtruse patent specifications or miscellaneous technical contributions often contradictory—has actuated the author to endeavor to present all available information, and in such logical sequence that every phase of the art which has received serious consideration may be found enumerated herein, and its stage of transition clearly indicated.

It will be noted that in addition to the original literature or patent citation, there is often included one or more abstract references to the original, the subject being to increase the efficiency of the work by indicating the various sources at which the particular ences to the original, the object being to increase the efficiency of to procure the original, may yet be able to obtain further information from the abstract references.

Those familiar with literary search will recall that often where the earlier chemical encyclopedias and dictionaries happen to make an error in citation, authors in succeeding years copy the inaccuracy without apparently taking the time or trouble to verify the accuracy of the reference or information from consultation of the original repository. In this manner inaccuracies in Jahr. and Centr. have been accepted and transmitted verbatim through the works of succeeding years, and copied from one work to another

without verificaton. In contradistinction to the above, the author with comparatively few exceptions has personally verified the references cited herein by consultation of the original periodicals.

While the manufacturing processes have been recorded in detail with unsparing frankness, yet there has been preserved that protection to manufacturers which chemical ethics demands.

Grateful appreciation is acknowledged to The Linotype Composition Company for linotype composition, and to the Rose Press (both) of Newark, New Jersey, for the presswork of this volume, for what must be conceded as a difficult and intricate piece of typography, and indebtedness to Messrs. John W. Bruce, F. C. S., and Dean S. Worden for compilation of the Patent and Name Indices respectively. The Subject Index was prepared by Mr. Leo Rutstein, who also read the entire work in proof. To these gentlemen much credit is due.

Many an otherwise valuable work has been materially impaired by the incompleteness, brevity or faulty construction of the index—without question the most important portion of a technical work—for recorded informaion becomes practically valueless when rendered unavailable or inacessible by omission in the index. In the herein recorded 3272 citations of 1596 patents, 2168 citations of 1292 investigators, and 6334 references of 5039 separate topical headings, a painstaking attempt has been made to adequately cover the subject matter of the work.

The author would greatly appreciate suggestions and criticisms from readers of this work, with a view to extending its usefulness in a possible future edition.

EDWARD CHAUNCEY WORDEN, FIRST.

Millburn, New Jersey, May 13th, 1915.

Table of Contents.

CHAPTER I.

Raw Materials.

Starch 2501
Cellulose 2501
Cotton 2503
Methylation and Ethylation of Cellulose..... 2505
Acetolysis and Octa-Acetyl-cellobiose 2509
Formic Acid..... 2516
Acetic Acid..... 2520
Acetic Anhydride..... 2526

CHAPTER II.

Manufacture of Cellulose Esters.

Historical 2530
Investigations of Stein..... 2541
Chemistry 2544
Cellulose Mono-acetate 2545
Cellulose Diacetates 2545
Cellulose Triacetates 2545
Cellulose Tetracetate 2547
Cellulose Pentacetate 2549
Theory of Acetylation..... 2550
Methods of Manufacture... 2552
Superficial Acetylation of Cellulose 2555
Acetylation of Modified Cellulose 2555
Commercial Manufacture of Partially Hydrated, Acetone-soluble Cellulose Acetate 2567
Other Partial Hydration Processes 2576
Acetation with Sulfuric Acid Containing Catalyzers.... 2586
Manufacture of Cellulose ..Acetate With Zinc Chloride 2598
Acetation with Substituted Acetic Acids..... 2600
Acetation in Presence of Chlorides 2601
Acetation without Apparent Change in Structural Form 2604
Purification 2610
Bleaching Acetated Cellulose 2611
Recovery of Acetic Anhydride and Acid..... 2612
Acetates of the Carbohydrates 2614
Cellulose Formate 2616
Cellulose Propionates 2634
Cellulose Butyrates 2639
Starch Formate 2641
Starch Acetate 2642
Cellulose Aceto-Nitrates ... 2648
Cellulose Aceto-Sulfates ... 2653
Cellulose Benzoates 2654

CHAPTER III.

Cellulose Acetate Solvents, Non-solvents and Plastic-Inducing Bodies.

Alcohols 2662
Ethers 2670
Aldehydes 2672
Ketones 2674
Acids 2680
Esters 2682
Nitro and Amido Solvents.. 2697
Essential Oils 2704
Other Cellulose Ester Plastic-inducing Bodies..... 2704
Diacetone Alcohol..... 2717
Solvent Recovery..... 2718
Wood Oil 2719
Hydrocarbon Chlorides..... 2719
Chloroform 2720
Carbon Tetrachloride..... 2721
Dichlorethylene 2725
Trichlorethylene 2728
Perchlorethylene 2734
Chlorhydrins 2735

Tetrachlorethane 2739
Pentachlorethane 2751
Hexachlorethane 2754
Benzine and Benzene..... 2755

CHAPTER IV.

Commercial Application of the Uninflammable Cellulose Esters.

Cellulose Acetate Plastics.. 2660
Cellit 2774
Cellon, Sicoid..... 2783
Sericose 2785
Boroid and Cellolite..... 2789
Acetate Lacquers..... 2789
Acetate Bronzing Liquids.. 2801
Imitation Gold Leaf..... 2802
Gilded Lace..... 2803
Treating Linen with Cellulose Acetate..... 2804
Cellulose Acetate Imitation Leather 2807
Cellulose Acetate Compound Fabrics 2811
Coating of Skins with Cellulose Acetate..... 2814
Artificial Bristles..... 2815
Preservation of Documents with Acetate Lacquers... 2816
Artificial Filaments from Cellulose Acetate..... 2817
Bayko Yarn..... 2825
Artificial Horsehair..... 2829
Microscopy of Acetate Silk.. 2830
Strengthening Artificial Filaments 2834
Artificial Sponge..... 2834
Dyeing Cellulose Acetate... 2835
Carbon Filaments from Cellulose Acetate..... 2845
Acetylated Cellulose in the Explosives Industry..... 2846
Cellulose Acetate as Insulating Material..... 2847
Cellulose Acetate for Toughening Incandescent Mantles 2855
Acetic Collodion..... 2856
Cellulose Acetate Photographic Emulsions..... 2857
Acetylcellulose Sheets..... 2860
Continuous Photographic Films 2864
Waterproofing Acetate Films 2869
Automobile Wind Shields... 2871
Testing Acetate Films..... 2871
Utilization of Waste Acetate Films 2874
Chronophotography, Motography 2876
Cellulose Acetate Window Panes 2879
Cellulose Acetate Phonograph Records 2879
Capping Bottles with Cellulose Acetate..... 2881
Cellulose Acetate in Air-Craft Manufacture..... 2882
Coating Cigar Tips..... 2887
Cellulose Acetate in Pharmacy 2888
Solidified Alcohol..... 2890
Feculose 2893

CHAPTER V.

Analysis of Uninflammable Cellulose Esters.

Estimation of Formic Acid. 2905
Acetic Acid..... 2907
Congealing Points of Acetic Acid 2908
Acetic Anhydride 2910
Acidity of Mixtures of Acetic Acid and Anhydride..... 2911
Calculation of Acetic Anrydride by Titration..... 2913
Index of Refraction..... 2914
Density of Acetic Acid..... 2914
Refractometric Determination of Acetic Anhydride. 2915
Estimation of Mixed Acetic Acid and Acetic Acid Anhydride by means of Density Determination..... 2916
Method of Menschutkin and Wasiljeff 2917
Analysis of the Cellulose Acetate. Moisture, Ash, Solubility 2917
Viscosity 2918
Tensile Strength 2919
Stability Tests 2919
Determination of the Copper Number 2920

Determination of Acid Radicals 2921
Method of Green and Perkin 2921
Method of Ost..... 2922
Sodium Ethylate Method... 2923
Method of Barthelemy..... 2924
Modification of Eberstadt... 2925
Determination of Combined Sulfuric Acid..... 2926

CHAPTER VI.

Appendix.

Acetates of Starch..... 2933
Recent Investigations 2955
Errata 2959
Index of Patents..... 2961
Index of Names..... 2975
Index of Subjects.... 2989-2930

LIST OF ILLUSTRATIONS.

Fig.		Page
501.	Acetylation of Cellulose (Pinay Method)	2609
502.	Thomson and Callan Process for Insulation with Cellulose Acetate	2848
503.	Film Coated Wire (Callan Process)	2852
504.	Bonwit Process of Film Formation	2868

LIST OF TABLES.

Table		
I.	Congealing Points of Concentrated Acetic Acid	2908
II.	Acidity of Mixtures of Acetic Acid and Acetic Anhydride	2911
III.	Calculation of Acetic Anhydride by Titration	2913
IV.	Refractometric Determination of Acetic Anhpdride	2915
V.	Estimation of Mixed Acetic Acid and Acetic Acid Anhydride by Means of Density Determinations	2916
VI.	Formulas for Acetylcelluloses	2933
VII.	Acetylation of Starch	2951
VIII.	Yield from Five Grams Dry Starch	2952
IX.	Acetylation of Cellulose	2953
X.	Yield from Five Grams Dry Cellulose	2954

ABBREVIATIONS.

A.A.A.S	American Association for the Advancement of Science.
Anon.	Anonyme
A.O.A.C	Association of Official Agricultural Chemists
abs.	absolute
Act.	Actien
Add.	Addition Patent
alc.	alcohol ethyl
alk.	alkaline
amp.	ampere
amt.	amount
approx.	approximate
at.	atom, atomic
atm.	atmosphere(s)
atm. pr.	atmospheric pressure
as-	asymmetric
av.	average
b.	boil(s), boiling
b. pt.	boiling point
c.	asymmetric carbon atom
cal.	calorie
cc.	cubic centimeter
chem.	chemical
com.	commercial
comp.	composition
compd.	compound
conc.	concentrat-ed, ion
cor.	corrected
c.p.	candle power
crys.	crystals, crystallized
cu.m.	cubic meter
cwt.	hundredweight
d-	dextro
d.	density
dil.	decimeter
dr.	dilute
dem.	dram
fl.	fluid
Farb.	Farbenfabriken
f. pt.	freezing point
gal.	U. S. gallon, 3785 cc.
Ges.	Gesellschaft
gm.	gram (s)
gr.	grains
hr.	hour(s)
insol.	insoluble
in.	inch
k.	kilogram
kw.	kilowatt
l.	liter(s)
l-	laevo
lab.	laboratory
Ltd.	Limited
m.	meter
m-	meta
mfr.	manufacturer
mfg.	manufacturing
mgm.	milligram
min.	minute(s)
mm.	milimeter
mol.	molecule(s)
mol. wt.	molecular weight
m. pt.	melting point
nor.	normal
o-	ortho
ord.	ordinary
oz.	Avoirdupois ounce
p-	para
pp.	precipitate
p.	pint
qt.	quart
quant.	quantitative
rechyst.	recrystallized
sat.	saturate(d)
sc.	scruple
sec.	second(s)
soln.	solution
Soc.	Societe
sp. gr.	specific gravity
sq.	square
sym-	symmetrical
temp.	temperature(s)
v-	vicinal
vac.	vacuum
vol.	volume(s)
wt.	weight
°	degrees Centigrade
%	percent by weight

TABLE OF SUMMARIES TO VOLUME EIGHT.

Chapter	Pages	Foot Notes	Number of References to			
			Patents	Names	Subjects	Literature
I	29	102	195	212	455	674
II	129	364	848	459	1,356	1,486
III	100	482	1,462	482	1,689	2,450
IV	147	322	595	449	2,333	839
V	22	27	26	73	176	113
VI	31	67	35	89	221	82
Total....	458	1,364	3,161	1,764	6,230	5,644

ABBREVIATIONS OF REFERENCES TO LITERATURE

A.	The Analyst
Acad.	Mémoires de l'Académie des Sciences
Agr. Gaz. N. S. W.	Agricultural Gazette of New South Wales, The
Agr. Ledg.	Agricultural Ledger
Agr. J. India	Agricultural Journal of India
Algem. Syn. Suikerfab. Ned. Ind.	Algemeen Syndicaat van Suikerfabrikanten in Nederl.-Indie. With Arch- Suikerind., etc.
Algem. Zts. Bierbrau	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation
Algem. Forst-u Jagd-Zeit.	Allgemeine Forst-und Jagd-Zeitung
Algem. Gerber-Zeit.	Allgemeine Gerber-Zeitung
Algem. Zeit. Bierbr. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation
Alk.	Alkohol
Am. Annual Phot.	American Annual of Photography
Am. Apoth. Z.	Deutsch-Amerikanische Apotheker Zeitung
Am. Brewers Rev.	American Brewers Review
Am. Chem.	American Chemist
Am. Chem. J.	American Chemical Journal
Am. Drug	American Druggist and Pharmaceutical Record
Am. Electrochem. Soc.	American Electrochemical Society
Am. Fertilizer	American Fertilizer, The
Am. Food J.	American Food Journal
Am. Gas Light J.	American Gas Light Journal, The
Am. J. Med. Sci.	American Journal of the Medical Sciences
Am. J. Pharm.	American Journal of Pharmacy
Am. J. Physiol., Boston	American Journal of Physiology, Boston
Am. J. Pub. Health	American Journal of Public Health
Am. J. Sci.	American Journal of Science
Am. Mach.	American Machinist
Am. Med.	American Medicine
Am. Mon. Micr. J.	American Monthly Microscopical Journal
Am. Nat.	American Naturalist
Am. Perfumer	American Perfumer and Essential Oil Review, The
Am. Phot.	American Photography
Am. Sugar Ind.	American Sugar Industry and Beet Sugar Gazette, The
Am. Vet. Rev., N. Y.	American Veterinary Review, New York
Anales agron.	Anales agronomicos
Anales. fis. quim.	Anales de la sociedad espanola de fisica y quimica
Anales. inst. med. nacional	Anales del instituto medico nacional
Anat.	Anatomie
Anat. Anzeig.	Anatomische Anzeiger
Ann.	Liebig's Annalen der Chemie

Ann.Bot.	Annals of Botany
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie
Ann. Chim. farm.	Annali di chimica e de farmacologia
Ann. Chim. Phys.	Annales de Chimie et de Physique
Ann. hyg. pub.	Annales d'hygiene publique
Ann. Inst. Pasteur	Annales de l'Institut Pasteur
Ann. mines	Annales des mines
Ann. Pharm.	Annales de Pharmacie, Louvain
Ann. Phil.	Annals of Philosophy
Ann. Physik.	Annalen der Physik
Ann. Rep., U. S. Dept. Agric.	Annual Report of the United States Department of Agriculture
Ann. R. Staz. Chim. Agrar. Sperim. Roma.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma
Ann. sci. agron.	Annales de la science agronomique francaise et étrangére
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy
Ann. Surg.	Annals of Surgery
Apoth.	Apothecary, Boston
Apoth. Ztg., Berl.	Apotheker Zeitung, Berlin
Apoth. Ztg., N. Y.	Apotheker-Zeitung, Deutsch-Amerikanische (N. Y.)
Appret.	Appreturzeitung
Arb. Gsndhtsamte., a.d.k. Berl.	Arbeiten aus den kaiserlichen Gesundheitsamte Berlin
Arb. a.d. pharm. Inst. D. Univ. Berl.	Arbeiten aus dem pharmazeutischen Institut der Universität Berlin
Architect and Eng.	Architect and Engineer
Arch. Anat. Phys.	Archiv für Anatomie, Physiologie und Wissenschaftliche Medicin
Arch. belges de méd. mil.	Archives belges de médicine militaire
Arch. biol.	Archives de biologie
Arch. Chem. u. Mikros.	Archiv Chemie und Mikroskopie
Arch. Entwickl. Organ.	Archiv fuer Entwicklungsmechanik der Organismen
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie
Ann. Falsif.	Annales des Falsifications
Arch. Farmacol. sper. Roma,	Archivio di Farmacolagia sperimentale e Scienze affini, Roma
Arch. fisiol.	Archivio di fisiologia
Arch. ges. Physiol.	Archiv für die gesammte Physiologie des Menschen und der Thier (Pflüger)
Arch. Hyg.	Archiv für Hygiene
Arch. Internal Med.	Archives of Internal Medicine
Arch. intern. pharmacodyn.	Archives internationales de pharmacodynamie et de therapie
Arch. intern. physiol.	Archives internationales de physiologie
Arch. ital. biol.	Archives italiennes de biologie
Arch. kinderheilk.	Archiv für kinderheilkunde
Arch. med. exp.	Archives de medicine experimentale et d'anatomie pathologique
Arch. Mikr. Anat Entwick.	Archiv für mikroskopische Anatomie (Entwicklungsgeschichte)

Arch. Néerland.	Archives Néerlandaises des sciences exacts et naturelles
Arch. path. Anat.	Archiv für pathologische Anatomie und Physiologie und für klinische Medizin (Virchow's)
Arch. d. Pharm.	Archiv de Pharmazie, Berlin
Arch. f. Pharm. og Chem. Copenhagen	Archiv for Pharmaci og Chemi, Copenhagen
Arch. sci. med.	Archivio per les scienze mediche
Arch. sci. phys. nat.	Archives des sciences physiques et naturelles
Arch. Suikerind.	Archief Suikerindustrie in Nederlandsch-Indie
Arch. Verdauungs-krankh.	Archiv für Verdauungs-krankheiten
Arkiv. Kemi, Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi
Arkiv. Math. Astron. Fysik	Arkiv för Mathematik Astronomi och Fysik
Arms and Expl.	Arms and Explosives
Astrophy. J.	Astrophysical Journal
Atelier Phot.	Atelier des Photographen
Atti. accad. Lincei	Atti della reale accademia dei Lincei, rendiconti, classe di scienze fisiche, mathematiche e naturali
Atti. R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino
Atti. inst. incoragg. Napoli	Atti del r. instituto d' incoraggiamento di Napoli, Naples, Italy
Australas. J. Pharm. Melbourne	Australasian Journal of Pharmacy, Melbourne
Australian Sugar J.	Australian Sugar Journal
Aust. P.	Austrian Patent
Aust-Hung. P.	Austro-Hungarian Patent
B. M. and S. J.	Boston Medical and Surgical Journal
Baugew. Z.	Baugewerks-Zeitung
Bd. of Trade J.	Board of Trade Journal
Beitr. path. Anat.	Beiträge zur pathologische Anatomie und zur allgemeinen Pathologie
Belg. P.	Belgian Patent
Ber.	Berichte der Deutschen chemischen Gesellschaft
Ber. botan. Ges.	Berichte der Deutschen botanischen Gesellschaft
Ber. Klin. Wochenschr.	Berliner klinische Wochenschrift
Ber. pharm.	Berichte der Deutschen pharmazeutischen Gesellschaft
Ber. physik. Ges.	Berichte der Deutschen physikalischen Gesellschaft
Ber. hüttenm. Jahrg.	Berg-unds hüttenmännische Jahrbuch
Berz. Jahrsb.	Berzelius Jahresberichte
Beton u. Eisen.	Beton und Eisen.
Betterave	Betterave.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb
Biochem. Bull.	Biochemical Bulletin
Biochem. Zentr.	Biochemische Zentralblatt, Leipzig
Bio-Chem. J.	The Bio-Chemical Journal
Biochem. Zts.	Biochemische Zeitschrift
Biol. Bull.	Biological Bulletin
Biol. Zentr.	Biologische Zentralblatt
Biophys. Centr.	Biophysikalische Zentralblatt, Leipzig
Blätter Zuckerrüb.	Blätter für Zuckerrübenban
Boll. chim. farm.	Bolletino chimico farmaceutico, Milan

Boll. estac. agr. Cindad Juarez.	Boletin de la estaciòn agricola experimental de Cindad Juarez.
Boll. ing.	Boletin de ingenieros
Bot. Zentr.	Botanisch Zentralblatt
Bot. Gaz.	Botanical Gazette
Bot. Jahrb. Engler.	Botanische Jahrbücher, Engler, Leipzig,
Bourse cuirs Liége	Bourse aux cuirs de Liége, bulletin hebdomadaire
Brass World	Brass World and Platers Guide, The
Braunk.	Braunkohle
Brewers, J. N. Y.	Brewers Journal, New York
Brenn. Ztg.	Brennerei Zeitung
Brewers' J. (Lon.)	Brewers' Journal and Hop and Malt Trades Review, The. (London)
Brick.	Brick.
Brick and Clay Record	Brick and Clay Record
Brit. Clay Worker	British Clay Worker, The
Brit. & Col. Drug.	British and Colonial Druggist, London
Brit. Food J.	British Food Journal
Brit. J. Almanac	British Journal Almanac
Brit. J. Dent. Sci.	British Journal of Dental Science
Brit. J. Phot.	British Journal of Photography
Brit. Med. J.	British Medical Journal
Bull. Acad. Med.	Bulletin of the Academy of Medicine
Bull. soc. Romane Stiin.	Buletinul societâtii Romane de Stiinte
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences
Bull. Acad. Sci., Cracow	Bulletin international de l'Académie des Sciences de Cracovie
Bull. Acad. Sci., Petrograd	Bulletin de l'Académie Impériale des Sciences de Petrograd
Bull. Am. Inst. Mining Engi.	Bulletin American Institute of Mining Engineers
Bull. Am. Pharm. Assoc.	Bulletin of the American Pharmaceutical Association
Bull. assoc. chim. sucr. dist.	Bulletin de l'association des chemistes de sucrerie distillerie de France
Bull. Bur. Agr.	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases
Bull. Bur. Chem. U. S. Dept. Agric.	Bulletins, Bureau of Chemistry, U. S. Department of Agriculture
Bull. Bur. Standards	Bulletin of the Bureau of Standards
Bull. Col. School Mines	Bulletin of the Colorado School of Mines
Bull. Dept. Agric. Jamaica	Bulletin of the Department of Agriculture, Jamaica
Bull. Dept. Agr. Trinidad	Bulletin of Agricultural Information, Department of Agriculture, Trinidad
Bull. Geol. Inst. Univ. Upsala	Bulletin of the Geological Institute of the University of Upsala
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America
Bull. Hyg. Lab. U.S.P.H. and M. H. Surv.	Bulletins of the Hygie Laboratory, United States Public Health and Marine Hospital Service
Bull. Imp. Inst.	Bulletin of the Imperial Institute, London
Bull. Johns Hopkins Hosp.	Bulletin of Johns Hopkins Hospital
Bull. Mass. Inst. Tech.	Bulletin of the Massachusetts Institute of Technology

Bull. Mulh.	Bulletin de la société industrielle de Mulhouse
Bull. Musee	Bulletin du Musée de l'industrielle de Belgique
Bull. Pharm.	Bulletin of Pharmacy
Bull. Pharm. Sud-est	Bulletin de Pharmacie du Sud-est, Montpellier
Bull. Rouen	Bulletin de la société industrielle de Rouen
Bull. sci. acad. roy. Belg.	Bulletin de la classe des sciences, academie royal de belgique
Bull. sci. pharmacolog.	Bulletin des sciences pharmacologiques
Bull. Soc. Chim.	Bulletin de la Société Chimique de France
Bull. soc. chim. Belg.	Bulletin de la société chimique de Belgique
Bull. soc. d'Encourag.	Bulletin de la société d'Encouragement
Bull. soc. de med. de Gand.	Bulletin de la société de médecine de Gand
Bull. soc. franç. phot.	Bulletin de la Société Française de Photographie
Bull. Soc. franç. Min.	Bulletin de la Société Française de Mineralogie
Bull. Soc. geol. France	Bulletin de la société géologique de France
Bull. Soc. Ind. Mulh.	Bulletin de la société industrielle de Mulhouse
Bull. soc. ind. min.	Bulletin de la société de l'industrie minerale
Bull. soc. ind. Amiens	Bulletin de la société industrielle d'Amiens
Bull. soc. ind. du Nord	Bulletin mensuel de la société industrielle du Nord de la France
Bull. soc. ind. Rouen	Bulletin de la société industrielle de Rouen
Bull. soc. intern. elec.	Bulletin de la société internationale des electriciens
Bull. soc. pharm. Bord.	Bulletin de la société de pharmacie de Bordeaux
Bull. soc. roy. pharm.	Bulletin de la société royale de pharmacie de Bruxelles
Bull. soc. scient. med. Rennes	Bulletin de la société scientifique et médicale de l'ouest, Rennes
Bull. Torrey Bot. Club.	Bulletin of the Torrey Botanical Club, New York
Bur. Mines Bull.	Bureau of Mines Bulletin, Department of the Interior.
C. A. (Chem. Abst.)	Chemical Abstracts
C. N.	Chemical News
Can. Drug.	Canadian Druggist
Can. Eng.	Canadian Engineer, The
Can. P.	Canadian Patent
Can. Pat. Off. Rec.	Canadian Patent Office Record
Can. Pharm. J.	Canadian Pharmaceutical Journal and Pharmacal Gazette
Caout. et Gutta-p.	Caoutchous et la Gutta-percha
Casopis Cesketho Lekarnictura	Casopis Cesketho Lekarnitura
Cassier's Mag.	Cassier's Magazine
Castings	Castings
Cellule	La cellule
Cell. Ind.	Die Celluloid Industrie
Cement	Cement
Cement Age	Cement Age
Cement Eng. News	Cement and Engineering News
Cement Record	Cement Record
Centr. Allgm. Path. u. path.	Centralblatt für allgemeine Pathologie und pathologische
Centr. Bakt. ê	Centralblatt für Bakteriologie, Parasitenkunde und Infectionskrankheiten
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie
Centr. Z.	Centralblatt für die Zuckerindustrie

Céramique	Céramique, La.
Chamb. Comm. J.	Chamber of Commerce Journal
Chem. Drug.	Chemist and Druggist, London
Chem. Drug. Aus.	Chemist and Druggist of Australasia
Chem. Eng.	Chemical Engineer
Chem. Gaz.	Chemical Gazette, The
Chem. Ind.	Chemische Industrie
Chem. Listy	Chemicke Listy
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett-und Harz-Industrie
Chem. Soc. Quart.	Chemical Society Quarterly
Chem. Tech.	Chemiker-und Techniker-Zeitung
Chem. Tec. Rep.	Chemische-Technische Repertorium
Chem. Trade J.	Chemical Trade Journal and Chemical Engineer
Chem. Weekbl.	Chemisch Weekblad
Chemical World	Chemical World, The
Chem. Zentr.	Chemisches Zentralblatt
Chem. Ztg.	Chemiker Zeitung
Chem. Zts.	Chemische Zeitschrift
Chimiste	Chimiste, Le
Ciment	Ciment, Le
Clay Worker	Clay Worker, The
Cleveland Med. J.	Cleveland Medical Journal
Collegium	Collegium (Scientific technical supplement to Ledermark)
Colliery Guardian	Colliery Guardian and Journal of the Iron and Coal Trades
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences
Compt. rend. Soc. de biol., Par.	Comptes rendus des séances et mémoires de la Société de biologie, Paris
Comp. rend. trav. lab. Carlsberg	Comptes rendue du travaux du laboratoire de Carlsberg
Concrete	Concrete
Concrete Age	Concrete Age
Con. Constr. Eng.	Concrete and Constructional Engineering
Concrete Eng.	Concrete Engineering no longer published separately. Combined with Cement Age
Corr. Blatt. Schweiz. Aerzte	Correspondenz-Blatt für Schweizer Aerzte
Corresp. Zahn.	Correspondenzblatt für Zahnärzte
Crell. Ann.	Chemische Annalen für die Freude der Naturlehre, etc.
Crón. méd. mex.. Mex.	Crònica médica mexicana, México
Cuir	Cuir, Le
D. A. Apoth. Ztg. N. Y.	Deutsch - Amerikanische Apotherker Zeitung, New York
D. Buchdr. Ztg.	Deutsche Buchdrueker-Zeitung
D. R. P.	German Patent
Dent. Cos.	Dental Cosmos, Philadelphia
Dental Digest	The Dental Digest, Chicago
Deut. Arch. Klin. Med.	Deutsches Archiv. für Klinische Medizin
Deut. Mechan. Ztg.	Deutsche Mechanicher-Zeitung
Deut. med. Wochenschr.	Deutsches medizinische Wochenshrift
Deut. Zuckerind.	Deutsche Zuckerindustrie
Diamant, Ztg.	Diamant, Glas-Industrie Zeitung
Dietet. Hyg. Gaz.	Dietetic and Hygienic Gazette, The

Ding. Poly.	Dinglers Polytechnische Journal
Drug. Circ.	Druggist's Circular
Drug Topics	Drug Topics, New York,
Dyer, Calico Ptr.	Dyer, Calico Printer, Bleacher, Finisher and Textile Review
E. P.	English (British) Patent
Eclectic M. J., Cincin.	Eclectic Medical Journal, Cincinnati
Eclectic Rev.	The Eclectic Review, New York
Econ. Geol.	Economic Geology
Edin. Med. J.	Edinburgh Medical Journal
Eisen Ztg. (Eisen Z.)	Eisen Zeitung
Elec. Rev.	Electrical Review
Elec. Rev. West. Elec.	Electrical Review and Western Electrician
Electr.	The Electrician
Elec. World	Electrical World
Electrochem. Met. Ind.	Electrochemical and Metallurgical Industry
Elektrochem. Zts.	Elektrochemische Zeitschrift
Elektrot. Zts.	Electrotechnische Zeitschrift
Engineer, The	Engineer, The
Eng. Contr.	Engineering and Contracting
Eng. Digest	Engineering Digest
Eng. Mag.	Engineering Magazine, The
Eng. Mining J.	Engineering and Mining Journal, The
Eng. News	Engineering News
Engng.	Engineering
Eng. Rec.	Engineering Record, Building Record and Sanitary Engineer
Engrais, L'.	Engrais, L'
Engl. Mech.	English Mechanic
Epicure	Epicure, The
Ergeb. d. Physiol.	Ergebnisse der Physiologie, Wiesbaden
Essig-Ind.	Deutsche Essigindustrie
Exper. Stat. Rec.	Experiment Station Record
F. P.	French Patent
Fachgenosse	Fachgenosse, Der
Färb. Ztg.	Deutsche Färber-Zeitung
Farben Ztg.	Farben Zeitung
Fer.	Ferrum, Halle
Field Mus. Nat. Hist. Chicago, Pub.	Field Museum of Natural History, Chicago, Publications
Flora	Flora
Földtani Közlöny	Földtani Közlöny
Folia Clin.	Folia clinica chimico et miscroscopica
Folia haematol.	Folia haematologica
Folia Therap., Lond.	Folia Therapeutica, London
Fortschr. Chem.	Fortschritte der Chemie, Physik und Physikalischen chemie
Fortschr. Med.	Fortschritte der Medizin
Foundry	Foundry, The
Frankfurter Zts. Pathol.	Frankfurter Zeitschrift für Pathologie
Freie K.	Freie Kunste
Gartenwelt	Gartenwelt, Die
Gas World	Gas World, The
Gaz. chim. ital.	Gazetta chimica italiana
Gaz. del Cliniche	Gazetta della Cliniche
Gaz. med. ital. lomb.	Gazetta medica italiana lombardia, Milano
Gaz. med. de Pav.	Gazetta medica de Pavia
Génie civ.	Génie Civil
Geol. Mag.	Geological Magazine

Geol. Survey, Can.	Geological Survey, Canada
Gerber	Gerber, Der
Gesundh. Ing.	Gesundheit-Ingenieur
Gew. Bl. Schw.	Schweizerisches Gerwerbeblatt
Gew. Bl. Würt	Gewerbeblatt aus Württemberg
Gew. Rechts. u. Urheb.	Gewerblicher Rechtsschutz und Urheberrecht
Gew. Ztg.	Wieck's Gewerbezeitung
Giorn. farm. chimi.	Giornale de farmacia, di chimica
Glasgow Med. J.	Glasgow Medical Journal
Glashütte	Glashütte, Die
Glas-Ind.	Glas-Industrie, Die
Glassworker	Glassworker. The
Glückauf	Glückauf, Berg-und Hüttenmannische Zeitschrift
Good Roads	Good Roads
Graph. Beob.	Graphischer Beobachter
Graph. Mitt.	Schweizer graphische Mitteilungen
Gummi-Ztg.	Gummi-Zeitung
Halle aux cuirs, La.	Halle aux cuirs, La.
Hahnemann. Month., Phila.	Hahnemannian Monthly, Philadelphia
Heart	Heart
Hide and Leather	Hide and Leather
Hung, P.	Hungarian Patent
Hutm. Ztg.	Deutsche Hutmacher-Zeitung
Hyg. Rundschau	Hygienische Rundschau, Berlin,
Hyg. viande	Hygiene de la viande et du lait, L'
Illumin. Eng. (London)	Illuminating Engineer (London), The
Illust. landw. Ztg.	Illustrierte landwirtschaftlic he Zeitung
Illust. Offi. J.	Illustrated Official Journal -The (Patents)
Impr.	L'imprimerie
Index Med.	Index Medicus, Washington
Ind. Chim.	Industria chimica
Ind. Ztg.	Deutsche Industrie Zeitung
India Dept. Agr.	India Department of Agriculture, Publications
India Rub. J.	India Rubber Journal
India Rub. World	India Rubber World
Ind. Text.	L'industrie textile
Intern. Beitr. Path. Therap.	Internationale Beiträge zur Pathologie uud Therapie die Ernährungsstörungen Stoffwechsel und Verdauungkrankheiten
Intern. Sugar J.	International Sugar Journal, The
Intern. Zts. Metall.	Internationale Zeitschrift für Metallographie
Intern. Zentr. Bauk-eram. Glasind.	Internationales Zentralblatt für Baukeramik und Glasindustrie
Inv.	Inventor's Record, The
Iron Age	Iron Age
Iron Coal Trades Rev.	Iron Coal Trades Review
It. P.	Italian Patent
J. A. C. S.	Journal American Chemical Society
J. Adv. Therap.	The Journal of Advanced Therapeutics, New York
J. Agr. Sci.	Journal of Agricultural Science
J. agr. tropicale	Journal d'agriculture tropicale
J. Agr. (Victoria)	Journal of the Department of Agriculture (Victoria, Australia)
Jour. Can. Min. Inst.	Journal of the Canadian Mining Institutes
Jahrb. Kinderheilk.	Jahrbuch für Kinderheilkunde und physische Erziehung

Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band
Jahrb. Phot.	Jahrbuch für Photographie und Reproduktionstechnik
Jahrb. Radioactiv. Electronik	Jahrbuch der Radioaktivität und Electronik
Jahrb. wiss. Bot.	Jahrbücher für wissenschaftliche Botanik
Jahr. Chem.	Jahresbericht der Chemie
Jahr. Pharm.	Jahresbericht der Pharmacie
Jahr. Phot.	Jahresbericht der Photographie
Jahr. Physiol.	Jahresbericht über die Fortschritte der Physiologie
Jahr. rein Chem.	Jahresbericht der rein Chemie
Jahr. ü. Tier-Chem.	Jahresbericht über die Fortschritte der Tier-Chemie
J. Allied Soc.	Journal of the Allied Societies, The [Dental]
J. Am. Lea. Chem. Soc.	Journal of the American Leather Chemists' Association
J. Am. Med. Assoc.	Journal of the American Medical Association
J. Am. Pharm. Assoc.	Journal of the American Pharmaceutical Association
J. Am. Soc. Mech. Eng.	Journal of the American Society of Mechanical Engineers
J. Analyt. Chem.	Journal of Analytical Chemistry
J. Appl. Micr.	Journal of Applied Microscopy
Jap. P.	Japanese Patent
J. Assoc. Eng. Soc.	Journal of the Association of Engineering Societies
J. Biol. C.	Journal of Biological Chemistry
J. Buchdr.	Journal für Buchdruckerkunst
J. Cam. Club	Journal of the Camera Club
J. Can. Mining Inst.	Journal of the Canadian Mining Institute, The
J. Chem. Met. Soc. S. Af.	Journal of the Chemical, Metallurgical and Mining Society of South Africa
J. chim. méd.	Journal de chimie médicale, de pharmacie et de toxicologie
J. chim. phys.	Journal de chimie, physique, electrochimie, theromchimie, radiochimie, mécanique chimie, stoechiométrie
J. Coll. Agr. Imp. Univ. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo
J. Coll. Agr. Tohoku Imp. Univ.	Journal of the College of Agriculture, Tohoku Imperial University
J. C. S.	Journal of the Chemical Society, London
J. Gas Light	Journal of Gas Lighting
J. de l'Anat.	Journal de l'anatomie et de la Physiologie normales et pathologiques de l'homme et des animaux
J. de Microgr.	Journal de microgra
J. Exper. Med.	Journal of Experimental Medicine
J. Exp. Zool.	Journal of Experimental Zoology, The
J. fabr. sucre	Journal des fabricants de sucre
J. Frank. Inst.	Journal of the Franklin Institute
J. Gasbel.	Journal für Gasbeleuchtung und verwandte Beleuchtungsarten

J. Gas Lighting	Journal of Gas Lighting, Water Supply and Sanitary Improvement
J. Geol.	Journal of Geology
J. Goldschm.	Journal der Goldschmiedekunst und verwandter Gewerbe
J. Home Econ.	Journal of Home Economics, The
J. Hygiene	Journal of Hygiene
J. N. E. Water Works Asso.	Journal New England Water Works Association
J. Path. Bact.	The Journal of Pathology and Bacteriology
J. pétrole	Journal du pétrole
J. pharm.	Journal de pharmacie
J. pharm. Anvers	Journal de pharmacie d'Anvers
J. pharm. chim.	Journal de pharmacie et de chimie
J. pharm. et chim.	Journal de pharmacie et de chimie, Paris
J. pharm. Elsass-Lothringen	Journal der Pharmacie von Elsass-Lothringen
J. Pharm. Soc. Japan	Yakugakuzasshi (Journal of the pharmaceutical society of Japan)
J.Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry
J. Infect. Dis.	Journal of Infectious Diseases
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Metals	Journal of the Institute of Metals
J. Iron Steel Inst.	Journal of the Iron and Steel Institute
J. Landw.	Journal für Landwirtschaft
J. Med. Paris	Journal de médicine de Paris
J. Med. Res.	Journal of Medical Research
J. mines met.	Journal des mines et de metallurgie
J. Morphology	Journal of Morphology
J. Nav. Eng.	Journal of Naval Engineers
J. Pharmacol. Exper. Therap.	Journal of Pharmacology and Experimental Therapeutics, Baltimore
J. Phot.	Journal of Photography
J. Phot. Suppl.	Journal of Photographic Supplies
J. Phys. Chem.	The Journal of Physical Chemistry
J. Physiol.	The Journal of Physiology
J. physiol. et path. gén.	Journal de physiologie et de pathologie géneral, Paris
J. physique	Journal de physique
J. prakt. chem.	Journal für praktische Chemie
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society
J. Roy. Astron. Soc. Canada	Journal of the Royal Astronomical Society of Canada
J. Roy. Inst.Pub.Health	Journal of the Royal Institute of Public Health
J. Roy. San. Inst.	Journal of the Royal Sanitary Institute
J. Roy. Soc. New South Wales	Journal of the Royal Society of New South Wales
J.Russ.Phys.Chem.Soc.	Journal of the Russian Physical Chemical Society
J. S. Arts	Journal of the Royal Society of Arts
J. S. C. I.	Journal of the Society of Chemical Industry
J.sci.math.physi.nat.	Jornal de sciencias mathematicas, physicas naturaes
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colorists
J. soc. pharm. Anvers	Journal de pharmacie, organe de la société de pharmacie d'Anvers
J. suisse chim. pharm.	Journal suisse de chimie et pharmacie
J. U. S. Artil.	Journal of the United States Artillery

Just's bot. Jahr.	Just's botanischer Jahresbericht, Leipzig and Berlin
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences
J. Western Soc. Eng.	Journal of the Western Society of Engineers
Kali	Kali
Keram. Rundschau	Keramische Rundschau
Koll. Chem. Beihefte	Kolloidchemische Beihefte
Kreutzer's Jahr. Phot.	Kreutzers' Jahresbericht Photographic
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar
Kühn-Archiv	Kühn-Archiv (formerly Berichte aus dem physiologischen Laboratorium und der Versuchsanstalt des Landwirthschaftlichen Instituts der Universität Halle
Kunst.	Kunststoffe
Lancet	The Lancet, London
Landw. Jahrb.	Landwirtschaftliches Jahrbücher (Zeitschrift f. wissenschaftliche Landwirtschaft)
Landw. Jahrb. Schweiz	Landwirtschaftliches Jahrbuch der Schweiz
Landw. Versuchs-Stat.	Die landwirtshaftlichen Versuchs-Stationen
Landw. Ztg. Fühling's	Landwirtschaftliche Zeitung, Fühling's
Leather	Leather
Leath. Mfr.	Leather Manufacturer
Leath. Tr. Rev.	Leather Trades Review
Leather World	Leather World, The
Lederind.	Lederindustrie (Deutsche Gerwer-Zeitung)
Ledermarkt	Ledermarkt, Der
Ledertech. Rund.	Ledertechnische Rundschau
Leipz. Färb. Ztg.	Leipziger Färber-und Zeugdrucker-Zeitung
Leipz.Monats.Text.Ind.	Leipziger Monatsschrift fuer Textil Industrie
Le Radium	Le Radium
L'Ind. Chim.	L'Industria Chimica
Letters on Brewing	Letters on Brewing
Lond. Phot. Soc.	London Photographic Society
Louisiana Planter	Louisiana Planter and Sugar Manufacturer, The
Lumière elec.	Lumière electrique, La
Lux. P.	Luxemburg Patent
Magyar Böripar	Magyar Böripar
Man. Build.	The Manufacturer and Builder
Maschinenb.	Der Maschinenbauer
Mat. grasses	Les Matières grasses
Medde. K. Vetenskapsakad. Nobel-inst.	Meddelanden från K. Vetenskapsakademiens Nobel-institut
Med. Klinik	Medizinische Klinik
Med. naturw. Arch.	Medizinisch-naturwissenschaftliches Archiv
Med. Rec.	Medical Record, New York
Med. Times	The Medical Times, London
Med. Wschr.	Medizinische Wochenschrift
Med. Ztg. Russl.	Medicinische Zeitung Russlands
Mem.Accad.Sci.Torino	Memorie della Reale Accademia delle Scienze di Torino
Mem. Coll. Sci. Eng. Kyoto	Memoirs of the College of Science and Engineering, Kyoto Imperial University
Mem. Imp. Min. Soc. Petrograd	Memoirs of the Imperial Mineralogical Society of Petrograd
Mem. Manch. Lit. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society
Mem. poudres	Memorial des poudres et salpêtres

Mem. r. accad. Lincei	Memorie della r. accademia dei Lincei, Classe di scienze fisiche, mathematiche e naturali
Mem. rev. soc. cien. "Antonio Alzate"	Memorias y revista de la sociedad cientifica "Antonio Alzate"
Mem. Soc. Nat. Kiev.	Memoirs of the Society Nat. Kiev. Kiév, Russia
Merck's Ann. Rep.	Merck's Annual Report
Merck's Arch.	Merck's Archives, New York
Merck's Rep.	Merck's Report
Metal Ind.	The Metal Industry
Metallurgie	Metallurgie
Met. Chem. Eng.	Metallurgical and Chemical Engineering
Met. italiana	Metallurgia italiana, La
Met. Tech.	Metal Technik
Mex. P.	Mexican Patent
Meyer Bro. Drug.	Meyer Brothers Druggist, St. Louis
Midland Drug.	Midland Druggist and Pharmaceutical Review
Milch Ztg.	Milch Zeitung
Milch. Zentr.	Milchwirtschaftliches Zentralblatt
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society
Mines and Minerals	Mines and Minerals
Mining Eng. World	Mining and Engineering World
Min. petrog. Mitt.	Mineralogische und petrographische Mitteilungen Tschermak's
Mining Sci.	Mining Science
Mining Sci. Press	Mining and Scientific Press
Mitt. k.k. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes
Mitt. Grenzg. der Med. Chir.	Mitteilungen aus den Grenzebieten der Medizin und Chirurgie
Mitt. Kgl. Materialprüfungsamt	Mitteilungen aus dem Königlichen Material prüfungsamt zu Gross Lichterfelde West
Mitt. Centralst. Wiss. techn. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlich technische Untersuchungen
Mitt. kgl. Prüfungsans. Wasser versorgung	Mitteilungen aus dem königlichen Prüfungsanstalt für Wasser versorgung und Abwässer beseitgung zu Berlin
Mitt. Lebensm. H.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene veröffentlicht vom Schweiz Gesundheitsamt
Mitt. Malerei	Technische Mitteilungen für Malerei
Mitth. Zool. Sta. Neapel	Mittheilungen aus der zoologischen Station zu Neapel, etc.
Mod. Sugar Planter	Model Sugar Planter, The
Mois chim. electrochim.	Mois chimique et electrochimique, Le
Mois min. met.	Mois minier et metallurgique, Le
Mois sci. ind.	Mois scientifique et industriel, Le
Monats.	Monatshefte für Chemie und verwandte Teile andere Wissenschaften
Monats. Chem.	Monatshefte für Chemie, Vienna
Monats. p, Dermatol.	Monatshefte für praktische Dermatologie
Mon. céram. verr.	Moniteur de la céramique de la verrerie et journal du céramiste et du chaufournier(réuins)
Mon. Sci.	Moniteur Scientifique
Mon. teint.	Moniteur de la teinture des apprêts et de l'impression des tissus
Mon. Text. Ind.	Leipziger Monatsschrift für Textil-Industrie
Monthly Cons.	Monthly Consular and Trade Reports

Montreal Pharm.J.	Montreal Pharmaceutical Journal
Mov. Pict. W.	Moving Picture World
Münch.med.Wochschr.	Münchener medizinische Wochenschrift
Mun.ic. Eng.	Municipal Engineer
Munic. J. Eng.	Municipal Journal and Engineer
Must. Ztg.	Leipziger Färber Zeitung (Färberei Musterzeitung
Nachr. kgl. Ges. Wiss. Göttingen	Nachrichten von der königlichen Gesellschaft der Wissenschaften zu Göttingen. (Mathematische-physikaiische Klasse)
N. A. R. D. Notes	The Journal of the National Association of Retail Druggists, Chicago
Nat.	Nature
Nat. Disp.	National Dispensatory
Nat. Drug.	National Druggist
Nat. Eclect. M. Ass. Quart.	The National Eclectic Medical Association Quarterly. Cincinnati
Nat. Glass Budget	National Glass Budget
Nature	Nature
Naturw. Umschau Ztg.	Naturwissenchaftliche Umschau der Chemiker-Zeitung
Neues Jahr. Min. Geol.	Neues Jahrbuch für Mineralogie, Geologie und paläontologie and Beilageband
Neurol. Centralb.	Neurologische Centralblatt
New England Eng.	New England Engineer, The
New Hampshire San. Bull.	New Hampshire Sanitary Bulletin
New Idea	New Idea (The), Detroit
Nick.	The Nickelodeon
N. med. chir. Ztg.	Neue medicinisch-chirurgische Zeitung
N. O. M. and S. J.	New Orleans Medical and Surgical Journal
Northwestern Drug.	Northwestern Druggist (The), Minneapolis
Notices of Judgment, U. S. Dept. Agric.	Notices of Judgment, U. S. Department of Agriculture
Nouv. remèdes	Nouveaux remèdes, Paris
Nuovo Cim.	Il Nouvo Cimento
N. Y. Med. J.	New York Medical Journal
Oest. Chem. Ztg.	Oesterreichische Chemiker Zeitung
Oesterr.-ung. Z. Zuckerind.	Oesterreichisch-ungarischen Zeitschrift für Zuckerindustrie und Landwirtschaf
Oesterr. Z. Berg. Hüttenw.	Oesterreichische Zeitschrift für Berg- und Hüttenwesen
Off, Gaz.	Official Gazette United States Patent Office
Oil Colour. J.	Oil and Colourman's Trades Journal
Oil, Paint, Drug Rep.	Oil, Paint and Drug Reporter
Omaha Drug.	Omaha Druggist (The), Omaha
Orgelb.	Die Orgelbauzeitung
Oversigt K. Danske Vidensk. Selsk. Forh.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger
Pacific Drug Rev.	Pacific Drug Review. Portland
Pacific Pharm.	Pacific Pharmacist
Paper	Paper
Paper Making	Paper Making
Paper Mill	Paper Mill and Woodpulp News
Paper Tr. J.	Paper Trade Journal
Papier-Fabr.	Papier-Fabrikant, Der
Papier Ztg.	Papier Zeitung
Perf. Essent. Oil Rec.	Perfumery and Essential Oil Record

Petroleum	Petroleum
Petroleum Gaz.	Petroleum Gazette
Petroleum Rev.	Petroleum Review
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere
Pharm.	Pharmakologie
Pharm.-Ber. D. A. B.	Pharmakopoe-Bericht. Die vegetabilischen Drogen des Deutschen Arzneibuches 5. Ausgabe, Ceasar & Loretz, Halle
Pharm. Centralh.	Pharmazeutische Centralhalle für Deutschland
Pharm. Era	Pharmaceutical Era
Pharm. J.	Pharmaceutical Journal and Pharmacist
Pharm. Post	Pharmazeutische Post
Pharm. Weekblad	Pharmaceutisch Weekblad
Pharm. Ztg.	Pharmazeutische Zeitung
Pharm. Ztg. Russl.	Pharmazeutische Zeitung Russland
Pharm. Zts.	Pharmazeutische Zeitschrift
Philippine J. Sci.	Philippine Journal of Science
Phil. Mag.	Philosophical Magazine
Phil. Trans.	Philosophical Transactions of the Royal Society of London
Phot. Archiv	Photographische Archiv
Phot. Chronik	Photographische Chronik und allgemeine Photographen-Zeitung
Phot. Jour.	Wilhelm Horn's Photographische Journal
Phot. Korr.	Photographische Korrespondenz
Phot. Mag.	Photographic Magazine
Phot. Mitth.	Photographische Mittheilungen
Phot. News	Photographic News
Photo-Era	Photo-Era
Phot. Rundsch.	Photographische Rundschau und Photographische Centralblatt
Phot. Wochenbl.	Photographische Wochenblatt
Phot. Zentr.	Photographische Centralblatt
Phot. Ztg.	Deutsche Photographen-Zeitung
Phys. Rev.	Physical Review
Physik.-Chem. Zentr.	Physikalisch-chemische Zentralblatt
Physik. Zts.	Physikalische Zeitschrift
Plant World	Plant World, The
Poly. Not.	Polytechnische Notizblatt
Pogg. Ann.	Poggendorffs Annalen der Physik und Chemie
Pogg. Ann. Beibl.	Poggendorffs Annalen der Physik und Chemie Beiblätter
Pop. Sci. Mon.	Popular Science Monthly
Pottery Gazette	Pottery Gazette
Pottery and Glass	Pottery and Glass
Power	Power
Pract. Drug.	Practical (The) Druggist and Pharmaceutical Review of Reviews, New York
Print. Reg.	Printers' Register
Proc. Acad. Wetenschappen	Proceedings of the Academy of Wetenschappen
Proc. Am. Acad.	Proceedings of the American Academy of Arts Sciences
Proc. Am. Inst. Elec. Eng.	Proceedings of the American Institute of Electrical Engineers

Proc. Am. Micr. Soc.	Proceedings of the American Microscopical Society
Proc.Am.Pharm.Assoc.	Proceedings of the American Pharmaceutical Association
Proc. Am. Phil. Soc.	Proceedings of the American Philosophical Society
Proc. Am. Soc. Civil Eng.	Proceedings of the American Society of Civil Engineers
Proc. Am. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials
Proc.Am.Water Works Asso.	Proceedings of American Water Works Association
Proc. Ass. Off. Agric. Chem.	Proceedings of the Association of Official Agricultural Chemists, Washington
Proc. Australian Inst. Min. Eng.	Proceedings Australian Institute of Mining Engineers
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society
Proc. Chem. Soc.	Proceedings of the Chemical Society
Proc. Eng. Soc. Western Penn.	Proceedings of the Engineers' Society of Western Pennsylvania
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers
Proc. K. Akad.Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen et Amsterdam. Proceedings (English version)
Proc. Manch. Lit. Phil. Soc.	Proceedings of the Manchester Literary and Philosophical Society
Proc. N. W. D. A.	Proceedings of the National Wholesale Druggists Association
Proc.Phil.Soc.Glasgow	Proceedings of the Glasgow Philosophical Society
Proc. Physiol. Soc.	Proceedings of the Physiological Society
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh
Proc. Roy. Soc. Lon.	Proceedings of the Royal Society of London
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine
Proc. U. S. Naval Inst.	Proceedings of U. S. Naval Institute
Prog. agr. et viti.	Progres agricole et viticole
Progressive Age	Progressive Age
Publ. Carnegie Inst.	Publications of the Carnegie Institution of Washington
Public Health	Public Health
Publ. ind.	Publication industrielle des machines par Armengaud
Pulp Paper Mag. Can.	Pulp and Paper Magazine of Canada
Pure Products	Pure Products. Scientific Station for Pure Products, 50 E. 41st St., New York
Quar. J. C. Soc.	Quarterly Journal of the Chemical Society
Quar. J. exp. Physiol.	Quarterly Journal of experimental Physiology
Quar. J. Geol. Soc.	Quarterly Journal of the Geological Society
Quar. J. Med.	Quarterly Journal of Medicine
Quar. J. Micr. Soc.	Quarterly Journal of the Microscopical Society
Radium	Radium, Le
Rass. min.	Rassegna mineraria metallurgica e chimica
Rec. trav. Chim.	Recueil des travaux Chimiques des Pays-Bas et de la Belgique
Reimann's Ztg.	Reimann's Färberzeitung

Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli
Rend. soc. chim. itali.	Rendiconti della societa chimica italiana
Rep. Chem. Lab. Am. M. Ass.	Reports of the Chemical Laboratory of the American Medical Association, Chicago
Rep. Chim. pure	Repertorium
Rep. Council Pharm. & Chem.	Reports of the Council of Pharmacy and Chemistry, American Medical Association, Chicago
Rep. New York Bd. Pharm.	Report of the New York State Board of Pharmacy
Rep. H. M. Insp. Expl.	Report of His Majesty's Inspectors of Explosives
Répert. pharm.	Répertoire de pharmacie, archeives de pharmacie et journal de chimie médicale réunis
Rev. chim. ind.	Revue de chimie industrielle et La revue de physique et de chimie
Rev. chim. pure app.	Revista de chimica pure applicada
Rev. de Métallurgie	Revue de Métallurgie
Rev. gén. bot.	Revue générale le botanique
Rev. gén. chim.	Revue générale de chimie pure et apliquées
Rev. gén. lait	Revue générale du lait
Rev. gén. mat. color.	Revue générale de matierès colorantes et de leurs applications aux textiles
Rev. gén. sci.	Revue générale des sciences pure et appliquées
Rev. hyg. pol. sanitaire	Revue d'hygiene et de police sanitaire
Rev. ind.	Revue industrielle
Rev. ind. agr. Tucuman	Revista industrial y agricola de Tucuman
Rev. méd., Chile	Revista médica de Chile
Rev. Med. Cir. Habana	Revista de Medicina y Cirugia, Habana
Rev. med. franc. et etrang	Revue médicale française et étrangère
Rev. metal.	Revue de metallurgie. m 9 (3 paginations, mémoires, extraits. and brevet)
Rev. real acad. cien. Madrid	Revista de la real academia de ciencias de Madrid
Rev. soc. Hygi. aliment	Revue de la société scientifique d'Hygiéne alimentaire et de l'alimentation rationelle dé l'homme
Rev. phot,	Revue de photographie
Rev. Vit.	Revue Viticulture
Rock Products	Rock Products
Russian Ann. Geol. Min.	Russian Annual of Geology and Mineralogy
Russ. J. ex. Landw.	Russiches Journal für experimentelle Landwirtschaft
Russ. P.	Russian Patent
Sanitary Record	Sanitary Record and Journal of Municipal Engineering, The
School Mines Quart.	School of Mines Quarterly, The
Schuh Ind.	Schuh Industrie
Schweiz. Wochschr.	Schweizerisch Wochenschrift für Chemie und Pharmazie
Sci.	Science
Sci. Abs.	Science Abstracts
Sci. Am.	Scientific American
Sci. Am. Suppl.	Scientific American Supplement
Sci. et Ind. Bull. Roure-Bertrand Fils	Scientific et Industrial Bulletin Rour-Bertrand Fils
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society

Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society
Seifenfabr.	Seifenfabrikant, Der
Seifens. Ztg.	Seifensieder Zeitung und Revue über die Harz-Fett-und Oelindustrie
Semi-Ann. Rep. Schimmel & Co.	Semi-Annual Report, Schimmel & Co., Miltitz
Shoe Lea. Repr.	Shoe and Leather Reporter
Sitzungsber. K. Akad. München	Sitzungsberichte der königlich bayerischen Akademie der Wissenchaften zu München
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin
Sitzb. kais. Akad. Wiss. Wien. Abt. I, IIa, IIb, III	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wein (Mathematisch-naturwissenschaftliche Klass) Abteilungen I, IIa, IIb, III
Sitzb. kgl. preuss. Akad.	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften
Skand. Archiv Physiol.	Skandinavisches Archiv für Physiologie
Snelling's Phot. J.	Snelling's Photograpihsche Journal
Southern Pharm. J.	Southern Pharmaceutical Journal
Span. P.	Spanish Patent
Spatula	Spatula (The), Boston
Sprechsaal	Sprechsaal
Sprengst. Waffen Mun.	Sprengstoffe, Waffen und Munition
Stahl u. Eisen.	Stahl und Eisen Zeitschrift für das deutsche Eisenhüttenwesen
Staz. sper. agrar. ital.	Stazioni sperimentali agrarie italiane, Le
Sucr. Belge	Sucrerie Belge, La
Sucr. ind. colon.	Sucrerie indigene et colonaile, La
Suddeut. Apoth. Ztg.	Suddeutsche Apotheker Zeitung
Surveyor	Surveyor and Municipal and County Engineer, The
Svensk farm. Tidskr.	Svensk farmaceutisk Tidskrift, Stockholm
Svensk Kem. Tidskrift	Svensk Kemisk Tidskrift
Svenska Mosskulturför.	Svenska Mosskulturföreningens
Swiss P.	Swiss Patent
Tagb. Frankf. Naturf.	Tagblatt Frankfurter Naturf.
Techn. Gemeindeblatt	Technische Gemeindeblatt
Techniker	Deutsche Techniker Zeitung
Techn. Quart.	Technology Quarterly
Text. Am.	Textile American
Text. Col.	Textile Colorist
Text. Mfr.	Textile Manufacturer
Text. Rec.	Textile Recorder
Text. World Rec.	Textile World Record
Text. Färb. Ztg.	Textil und Färberei-Zeitung
Text. Ztg.	Textil Zeitung
Therap. Gaz.	The Therapeutic Gazette
Therapist	Therapist (The) London
Therap. Monats.	Therapeutische Monatshefte
Therap. Neuh.	Therapeutischen Neuheiten, Leipzig
Tijdschr. nijv.	Tidjdschrift ter bevordering van nijverhed
Tischl. Ztg.	Deutsche Tischlerzeitung
Tonind. Ztg.	Tonindustrie Zeitung
Trans. Acad. Sci. St. Louis	Transactions of the Academy of Sciences of St. Louis
Trans. Am. Ceram. Soc.	Transactions of the American Ceramic Society

Trans. Am. Electrochem. Soc.	Transactions of the American Electrochemical Society
Trans. Am. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers
Trans. Am. Inst. Homœop.	Transactions of the American Institute of Homœopathy, Philadelphia
Trans. Am. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers
Trans. Am. M. Ass., Sec. Pharm. and Therap.	Transactions of the Section on Pharmacology and Therapeutics of the American Medical Association
Trans. Am. Micr. Soc.	Transactions of the American Microscopical Society
Trans. Camb. Phil. Soc.	Transactions of the Cambridge Philosophical Society
Trans. Can. Inst.	Transactions of the Canadian Institute
Trans. English Ceram. Soc.	Transactions of the English Ceramic Society
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Geol. Soc. S. Africa	Transactions of the Geological Society of South Africa
Trans. Illum. Eng. Soc.	Transactions of the Illuminating Engineering Society
Trans. Kansas Acad. Sci.	Transactions of the Kansas Academy of Science
Trans. Mining Geol. Inst. India	Transactions of the Mining and Geological Institute of India
Trans. Nat. Eclec. M. Ass.	Transactions National Eclectic Medical Association, Indianapolis
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science
Trans. Path. Soc.	Transactions of the Pathological Society
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh
Trans. Roy. Soc. Lon.	Transactions of the Royal Society of London
Tropenpflanzer	Tropenpflanzer (Der), Berlin
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen
Uhland's Tech. Rund.	Uhland's Technische Rundschau
Umschau	Umschau, Die
Univ. Ill. Bull.	University of Illinois Bulletin
U. S. A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U. S. A.
U. S. A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U. S. A.
U. S. Disp.	United States Dispensatory
U. S. Geol. Sur.	United States Geological Survey
U. S. Nav. Inst. Proc.	United States Naval Institute Proceedings
U. S. Nav. Med. Bull.	United States Naval Medical Bulletin
U. S. P.	United States Patent
U. S. Ph.	United States Pharmacopoeia
Verh. Ges. deut. Naturforsch. Aerzte	Verhlandung der Gesellschaft deutscher Naturforscher und Aerzte
Verh. v. Gew. Sitz B.	Verhandlungen des Vereins zur Beförderung des Gewerbefleisses
Veröffent. kais. Gesundh.	Veröffentlichungen des kaiserlichen Gesundheitsamts
Vet. J. Lond.	Veterinary Journal, London

Viertelj. ger. Med.	Vierteljahreschrift für gerichtliche Medizin und öffentliches Sanitätswesen
Viertelj. Schr. f. Zahn.	Vierteljahrschrift
Virchow's Arch. f. path. Anat. u. Hist.	Virchow's Archiv. für pathologie, Anatomie und Histologie
Wag. Jahr.	Wagner's Jahrsbericht
Wasser u. Abwasser	Wasser und Abwasser
Water Supply Papers	Water Supply Papers
West. Chem. Metal.	Western Chemist and Metallurgist
West. Drug.	Western Druggist
West. Brewer	Western Brewer, The
Wiener klin. Wochschr.	Wiener klinische Wochenschrift
Wiener landw. Ztg.	Wiener landwirtschaftliche Zeitung
Wiener med. Wochschr.	Wiener medizinische Wochenschrift
Wiener Mitt. Phot.	Wiener Mitteilungen (Photographischen Inhalts)
Wiss. Abhandl. Phys.-Tech. Reichsanstalt	Wissenchaftliche Abhandlungen der Physikalish-Technischen Reichsanstalt
Wochbl. Papierfabr.	Wochenblatt der Papierfabriken
Wochsch. Brau.	Wochenschrift für Brauerei
Wochschr. Centr.-Ver. Rubezuker-ind.	Wochenschrift des Central-Vereins für Rubezuker-industrie in der Oesterr-Ung-Monarchie
Wollen Ztg.	Wollen Zeitung
World's Paper Trade Rev.	World's Paper Trade Review
Year-Book Pharm.,London	Year-Book of Pharmacy, London
Zahntech.	Die Zahntechnische Reform
Zentr. Biochem. Biophy.	Zentralblatt für Biochemie und Biophysik
Zentr. exp. Med.	Zentralblatt der experimentellen Medizin (former name Zentralblatt für die gesamte Physiologie und Pathologie des Stoffwechsels).
Zentr. inn. Med.	Zentralblatt für innere Medizin
Zentr. Physiol.	Zentralblatt für Physiologie
Zentr. Physiol. u. Path. d. Stffwchsls	Zentralblatt für die gesammte Physiologie und Pathologie des Stoffwechsels, Berlin und Wien
Zts. allgem. österr. Apoth.-Ver.	Zeitschrift des allgemeinen österreichischen Apotheker-Vereins
Zts. allgem. Physiol.	Zeitschrift für allgemeine Physiologie
Zts. anal. Chem.	Zeitschrift für analytische Chemie
Zts. ang. Chem.	Zeitschrift für angewandte Chemie, und Zentralblatt für technische Chemie
Zts. anor. Chem.	Zeitschrift für anorganische Chemie
Zts. Berg-Hütten Salinenw.	Zeitschrift für das Berg-Hütten- und Salinenwesen im Preussichen Staate
Zts. Biol.	Zeitschrift für Biologie
Zts. Botanik	Zeitschrift für Botanik
Zts. chem. Apparat.	Zeitschrift für chemische Apparatenkunde (Discontinued)
Zts. chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide
Zts. Chemotherap.	Zeitschrift für Chemotherapie und verwandte Gebiete. Erste Teil, Original; Zweite Teil, Referate. (Formerly Folia Serologia).
Zts. d. allg. österr. Apoth.-Ver., Wien.	Zeitschrift des allgemeinen österreichischen Apotheker-Vereines, Wien
Zts. deut. geol. Ges. A.	Zeitschrift der deutschen geologischen Gesellschaft A (abhandlungen)

Zts. Dreschler	Zeitschrift für Dreschsler, Elfenbeingraveure und Holzbildhauer
Zts. Elektrochem.	Zeitschrift für Elektrochemie
Zts. f. exper. Path. u. Therap.	Zeitschrift für experimentelle Pathologie und Therapie, Berlin
Zts. Färben-Ind.	Zeitschrift für Färben-Industrie
Zts. Feuerwehr.	Illustrirte Zeitschrift für die deutsche Feuerwehr
Zts. Fleisch. Milchhyg.	Zeitschrift für Fleisch- und Milchhygiene
Zts. ges. Brauw.	Illustrirte Zeitschrift das gesammte Brauwesen
Zts. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen
Zts. ges. Schies-Sprengstoffw.	Zeitschrift für die gesamte Schiess-Sprengstoffwesen
Zts. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten
Zts. Immunit. Abt. I. 13. Abt. Ref.	Zeitschrift für Immunitätsforschung und experimentelle. Therapie. Abteilung I. 13. Abteilung II. or Ref. 1 vol.
Zts. Induk. Abst. u. Vererbungslehre.	Zeitschrift für Induktive Abstammungs- und Vererbungslehre.
Zts. Instrumentenk.	Zeitschrift für Instrumentenkunde
Zts. Klin. Med.	Zeitschrift für Klinische Medizin
Zts. Krebsforschung	Zeitschrift für Krebsforschung
Zts. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie
Zts. landw. Versuchsw.	Zeitschrift für das landwirtschaftliche Versuchswesen in Oesterreich
Zts. Mikr. Tek.	Zeitschrift für Mikroscopischen Teknik
Zts. Nahr. Genuss. (Z. genuss)	Zeitschrift für Untersuchung der Nahrungs und Genussmittel, sowie der Gebrauchsgegenstände
Zts. öffentl Chem.	Zeitschrift für öffentliche Chemie
Zts. Pflanzenkrankheiten	Zeitschrift für Pflanzenkrankheiten
Zts. physik. C.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre
Zts. physik. Chem. Unter.	Zeitschrift für dem physikalischen und chemischen Unterricht
Zts. physiol. Chem.	Zeitschrift für physiologische Chemie (Hoppe-Seylers)
Zts. prakt. Geol.	Zeitschrift für praktische Geologie
Zts. Reprodukt.	Zeitschrift für Reproduktiontechnik
Zts. Spiritusind.	Zeitschrift für Spiritusindustrie
Zts. Ver. deut. Inge.	Zeitschrift des Vereins deutscher Iugenieure
Zts. Ver. Zuckerind.	Zeitschrift des Vereins der deutschen Zuckerindustrie
Zts. wiss. Mikr.	Zeitschrift für wissenschaftliche Mikroscopie
Zts. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie
Zts. wiss. Zool.	Zeitschrift für wissenschaftliche Zoologie
Zts. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen

CHAPTER I.

RAW MATERIALS.

DISREGARDING the numerous catalytic agents which have from time to time been proposed, but which are present in comparatively very small proportions, the materials entering into the formation of the various non-flammable esters of cellulose and starch, are but few in number. The process in its simplest form comprises the treatment of some form of normal or modified cellulose with a mixture of acetic acid and acetic anhydride in the presence of a minute amount of sulfuric acid, zinc chloride or other catalyzer, until the desired degree of acetylation has been reached, when the formed acetic ester is washed free from reacting chemicals and dried.

Starch, a vegetable product belonging to the group of carbohydrates, is usually prepared commercially from potatoes, wheat, maize or rice. Starch has been superficially or incompletely acetated for the formation of agglutinants and adhesives, but acetated starch is seldom, if ever, used in solution for non-inflammable lacquers or continuous photographic films. The starch acetates, in tensile strength, tenuity and film-forming ability are decidedly inferior to acetated cotton or tissue paper.

Cellulose,[1] like starch, chemically belongs to the group of polysaccharides, its constituent monose groups being mainly, if not entirely, composed of dextrose. Cellulose gives rise to a series of esters corresponding to the presence of three hydroxyl groups which possess both acid functions toward alkaline bases as characteristic of all saccharides, and are susceptible to a degredation of the cellulose complex under the influence of hydrolytic agents. Cellulose is a generic name applied

1. For exhaustive summary of the physical properties and chemical reactions of hydrocellulose, oxycellulose, and normal and modified cellulose, see Part One of this work. For mercerized cellulose, see Part Nine.

to a class of substances possessing many physical and chemical properties in common, rather than a specific name of a definitely characterized chemical individual. As a group, the celluloses are mostly colorless, chemically inert and odorless bodies, insoluble in all simple solvents without decomposition, and possessing the elementary composition indicated by the formula $C_6H_{10}O_5$ taken n times, n being usually regarded as 2. The constitution of cellulose—as yet undetermined—has been the subject of innumerable investigations, much of a contradictory nature. The reactions of cellulose are those of saturated compounds. Much information concerning the inner mechanism of the cellulose molecule has been obtained by acetolytic studies and the formation of the various biose acetates (which see).

Cellulose does not appear to originate as the product of the direct action of carbon dioxide and water upon the protoplasmic cell contents, but apparently through the mediation of starch and other simpler carbohydrates. H. Ost [1] has endeavored to differentiate between natural or normal cellulose and its modifications by means of viscosity determinations, chemically modified bodies giving solutions of lower viscosity than normal cellulose.[2]

P. Minck [3] obtains cellulose, especially the fibres from cottonseed hulls, suitable for the manufacture of cellulose acetate by a dry method and in a purely mechanical manner, the cellulose being so opened up as to remain undamaged, and not more reduced in length than is admissable for the industrial applications of esterification.

In the matter of producing stable acetated cellulose derivatives, perhaps because the finished product lacks the explosive force of the corresponding nitric esters, undoubtedly insufficient attention has been paid to the proper selection

1. Zts. ang. Chem. 1911, 24, 1892; abst. JCS 1911, 100, i, 838; Chem. Zentr. 1911, II, 1518; JSCI 1911, 30, 1247; CA 1912, 6, 684. He tested cuprammonium solutions of cellulose in a specially designed viscosimeter.

2. For the determination of water, ash, fat, oxycellulose and hemicellulose and the control of cellulose used in the manufacture of artificial silk, see C. Chevalier and A. Lejeune, Bull. assoc. inst. Meurice, 1, 250; Bull. soc. Belg. 27, 99; CA 1913, 7, 2312.

3. E.P. 12718, 1906.

and purification of the cellulose used in the formation of the esters. It would appear that just as discreet and careful supervision in the selection and purification is demanded as is customary at the present time in the selection of cellulose for conversion into smokeless powder and the manufacture of pyroxylin plastics typified by celluloid.

Cotton is the usual form of cellulose selected for acetation, and should be as carefully selected and prepared as if intended for nitration for smokeless powder manufacture. Raw cotton is first pulled out by means of a teasing machine, and after opening up, the wax and similar bodies are removed by scouring with sodium carbonate solution. The absence of dead cotton and unripe fibres should be determined by microscopical examination, and the scouring continued until the cotton is rendered sufficiently absorbent to readily sink in water when immersed therein. Degreasing of the cotton with solvents as benzine, carbon tetrachloride or trichlorethylene is seldom resorted to. After scouring, a light hypochlorite or sodium peroxide bleach renders the cotton in the receptive state for acetation. C. Piest has examined various cottons intended for nitration,[1] and determined the desired degree of bleaching.[2] According to T. Moreul,[3] the cellulose most suitable for the manufacture of the French smokeless powder, are short cotton fibres stripped from the seeds at the crushing plants, the immature and dead fibres having been removed during the cleaning process. C. Schwalbe[4] determines the degree of bleaching of cotton by means of the reduction of Fehling's solution, overbleached cotton reducing the solution, whereas

1. Zts. ang. Chem. 1912, **25**, 396; abst. Chem. Zentr. 1912, I, 1643; C.A. 1912, **6**, 1688. Chem. Ztg. 1913, **37**, 753; abst. JSCI 1913, **32**, 694; C.A. 1913, **7**, 3545; Chem. Zentr. 1913, II, 550.

2. Zts. ang. Chem. 1912, **25**, 2518; abst. Chem. Zentr. 1913, I, 1145; JCS 1908, **94**, 1, 138; CA 1913, **7**, 895. For action of water and alkali upon cotton cellulose, see C. Schwalbe and M. Robinoff, Zts. ang. Chem. 1911, **24**, 256; abst. Kunst. 1911, **1**, 452; CA 1911, **5**, 1838; Wagn. Jahr. 1911, II, 432; Chem. Zentr. 1911, I, 974; JCS 1911, **100**, i, 180; JSCI 1911, **30**, 277. See also Tauss, Dingl. Poly. 1889, **273**, 276; abst. Zts. ang. Chem. 1889, **2**, 531; Chem. Centr. 1889, II, 444; Jahr. Chem. 1889, 2838. M. Robinoff, Papierfabr. 1912, **10**, 968; abst. JSCI 1912, **31**, 867; CA 1913, **7**, 1414.

3. Bull. Sci. Pharmacolog. **20**, 101.

4. Chem. Ztg. 1907, **31**, 940; abst. CA 1908, **2**, 704; JSCI 1907, **26**, 1107. Faerb. Ztg. 1908, **19**, 33; abst. JSCI 1908, **27**, 156.

with pure cotton cellulose no such action takes place. F. Stewart[1] prepares cellulose suitable for esterification by taking a fine bleached pulp produced from the fibres and cellular matters obtained by the treatment of immature maize stems, which are bleached with hypochlorite solution and hydrochloric acid, and thoroughly washed. The Zellstoff-fabrik Waldhof[2] advocate the use of wood cellulose from the sulfite process, especially after fine comminution and pressing into flakes. Sulfite cellulose as raw material for esterizing, has been carefully investigated by K. Nitzelnadel[3] and by P. Girard.[4] The latter purifies wood pulp intended for artificial filament formation by extracting the disintegrated cellulose by a volatile resin solvent which is a non-solvent of cellulose, acetone, and chlorides of carbon being especially suitable. The solvents are preferably employed in conjunction with 5-10% of commercial aqueous formaldehyde solution.

F. Kilmer[5] has recorded in detail the methods of preparation of cotton fiber for surgical purposes, in which condition it is especially suitable for acetation, when deprived of substantially all of its atmospheric moisture. In the preliminary treatment of cellulose for technical purposes, E. Berl[6] advocates reducing the viscosity of the esterized cellulose, either by a depolymerization of the cellulose, mercerization, or regulated hydrolysis before esterification.

In general, wood pulp gives a thinner flowing solution after acetation than does cotton, and a solution which upon evaporation to dryness forms films of inferior strength. Wood pulp also acetates more readily and at a lower temperature, and for these reasons the amount of acetic anhydride in the

1. U.S.P. 1017023, 1912; abst. J.S.C.I. 1912, **31**, 279; C.A. 1912, **6**, 930.

2. It. P. 28964, 1891. A. Schindler, Jour. Soc. Dyers 1908, **24**, 106; abst. J.S.C.I. 1908, **27**, 497. O. Masson, Proc. Roy. Soc. 1904, **74**, 230; abst. J.S.C.I. 1904, **23**, 1143.

3. Wochenbl. Papierfabr. 1912, **43**, 3488; abst. J.S.C.I. 1912, **31**, 954; C.A. 1913, **7**, 257; Chem. Zentr. 1912, II, 2157.

4. F.P. 443897, 1912; abst. J.S.C.I. 1912, **31**, 1120.

5. J.S.C.I. 1904, **23**, 967.

6. Zts. ges. Schiess und Sprengstoffw. 1909, **4**, 81; abst. J.S.C.I. 1909, **28**, 380; C.A. 1909, **3**, 1926; Chem. Zentr. 1909, I, 1275; Jahr. Chem. 1909, 384; Chem. Tech. Rep. 1909, **33**, 194; Wagn. Jahr. 1909, I, 431.

acetylizing bath may be somewhat reduced. Acetated wood pulp appears to partially hydrate more readily than an ester prepared from cotton cellulose. The fact, however, that cotton waste is plentiful, can be readily procured and purified, and can be depended upon to produce an acetate satisfactory in respect to uniformity, solubility and film-forming capacity, gives cotton the preference over wood pulp at the present time as a source of cellulose for acetylation. It has been claimed that cotton produced in a cold, wet season, where the growth has been slow—as indicated by the thickened cellular wall and smaller inner filamentous canal—does not as readily esterify as a cotton grown in a locality more favorable as regards humidity and high temperature, where the microscopic examination of the filament shows a thin-walled tube and correspondingly larger lumen. In any event, the cellulose, either cotton or wood pulp, should be carefully and thoroughly dried at 105° immediately before acetation, and preferably introduced cold into the acetating mixture which should also be at room temperature. If the atmospheric moisture is not removed before immersion in the acetation bath, esterization takes place more speedily, there is a greater rise in temperature, and the difficulty of keeping the acetating bath under control is correspondingly increased. This is especially noticeable when working with larger quantities. Grass-bleached tissue paper similar to that used for nitration in pyroxylin plastic (celluloid) manufacture is an excellent form of cellulose for conversion into the acetate.

Methylation and Ethylation of Cellulose. L. Lilienfeld has recently described[1] ethers of cellulose or modified cellu-

1. E.P. 12854, 1912. F.P. 447974, 1912. Belg. P. 254591, 1912; abst. J.S.C.I. 1913, **32**, 420, 940; J.C.S. 1913, **108**, 1741; C.A. 1913, **7**, 3839; Mon. Sci. 1914, **80**, 3; Kunst. 1913, **8**, 195. See also E.P. 6035, 1913; abst. J.S.C.I. 1914, **33**, 417.

In E.P. 12854, 1912, are given twelve examples for manufacturing the various ethers comprehended in the patent. As original cellulosic material may be used either:—

(a) 3750 parts by weight of raw viscose containing about 300 parts by weight of cellulose and about 130-200 parts by weight of sodium hydroxide diluted with 3750 parts by weight of water. Heat on the water bath with stirring until complete coagulation takes place. The coagulated mass which has crumpled into small lumps by the stirring is thoroughly washed in flowing water, crushed,

lose prepared by substituting one or more of the cellulosic pressed to 5000 parts by weight, and then dissolved in 1000 parts of 50% sodium hydroxide.

(b) Hydrocellulose is precipitated by dilute sulfuric acid from solutions of cellulose in Schweitzer's reagent, then dissolved in caustic soda solution so that 120 parts of the solution contains 10 parts of hydrocellulose and 10 parts of caustic soda.

(c) Cellulose is heated with 30-50% caustic soda solution, the liquor poured off and the resulting hydrocellulose dissolved by the addition of water. This solution is filtered, precipitated by dilute sulfuric or acetic acid and the precipitated hydrocellulose dissolved in caustic soda so that 120 parts of solution contain 10 parts each hydrocellulose and sodium hydroxide.

Twelve hundred parts of (a), (b) or (c) containing 100 parts of cellulose or hydrocellulose and 100 parts of caustic soda are mixed with 100-400 parts of 30% caustic soda, well stirred and gently warmed. To this is then added 200 parts by weight of diethyl sulfate in small portions and the mixture again heated for a time if required. The turbid reaction mass is diluted with hot water, then acidulated with dilute vitriol to precipitate the ethyl-cellulose, which is further washed with water to neutrality and dried. Thus prepared the cellulose ether is a white, pulverulent or flaky substance, readily soluble in cold water, formic acid, hot or cold aqueous acetic acid and aqueous pyridine, but insoluble in alcohol and hot water.

Example 8 of the patent. Twelve hundred parts by weight of one of a primary solution as in foregoing example and containing 100 parts by weight of cellulose and 100 parts by weight of sodium hydroxide are mixed with 100 parts of 30% caustic soda solution and gently heated; 100-200 parts of diethyl sulfate is gradually added, the addition requiring from half to one hour. If necessary the mass is heated on the water bath for one to two hours, the reaction mixture allowed to cool, and rubbed with 300-600 parts of powdered caustic soda or an equivalent amount of caustic potash. Then the mass is again heated and into it is introduced 300-1300 parts by weight of diethyl sulfate in small portions, whereupon the cellulose ethyl ether separates, accompanied by a rise in temperature and a frothing of the mass. After dilution with water, the reaction mixture is acidulated with dilute vitriol or made alkaline, then filtered and washed free from reacting salts. The resulting white, amorphous, bulky powder is insoluble in hot or cold water, but readily soluble in the following solvents—methyl and ethyl alcohol, formic acid, glacial acetic acid, pyridine, quinoline, picoline, di-chlorhydrin, epichlorhydrin, nitrobenzene, methyl acetate, ethyl acetate, ethyl phthalate, ethyl sebacate, ethyl citrate, ethyl succinate, ethyl tartrate, amyl and butyl acetates, ethyl benzoate, ethyl succinate, acetone, pentachlorethane, tetrachlorethane, ethylene trichloride, acetylene dichloride, carbon tetrachloride, chloroform, benzene, toluene, xylene, phenol, nitrophenols, the cresols, naphthalene, aniline, toluidine, formanilid, acetanilid, turpentine oil, camphor, castor, linseed, olive and Chinese wood oils, stearine, beeswax, Japan wax, lanolin, nitromethane, phenyl ether, triphenyl phosphate, tricresyl phosphate, vaseline, camphor oil, paraffin oil, petroleum, naphtha, etc. Readily soluble in a mixture of ethyl alcohol and ether, less readily in ethyl ether alone. It can withstand heating for days in a digestor with water at temperatures as high as 170° without showing alteration. Can be heated for days with 25% aqueous caustic soda or with 25% alcoholic potash solution without undergoing decomposition.

hydroxyl hydrogen atoms by an alcoholic radical. The manner of preparation and range and variation in solubility, indicate the cellulose has undergone considerable degradation. In order to obtain these ethers, cellulose, preferably so modified as to be soluble in alkalis, is treated with the alkyl ester of an inorganic acid in the presence of a base. For example, cellulose soluble in alkali is prepared by regeneration from a solution of ordinary or modified cellulose, *e. g.*, from viscose, or from zinc chloride or cuprammonium cellulose solutions. To 1,200 parts of a solution of such cellulose, containing 100 parts of cellulose and 100 parts of caustic soda, are added 100 parts of a 30% caustic soda lye; the liquid is heated moderately and 100-200 parts of diethyl sulphate gradually added. The mixture is further heated for ½-2 hours on the water-bath, and, after cooling, 300-600 parts of dry powdered caustic soda are added with stirring. The mixture is again heated and treated again with 300 to 1,300 parts of diethyl sulphate in small portions at a time. The cellulose ether separates, the liquid is diluted, acidified, and the product collected. The ether thus prepared is insoluble in cold water, but soluble in a large number of organic solvents, and shows on analysis a composition corresponding to a pentaethyl cellulose ether (on the C_{12} basis). According to the conditions employed and the proportions of the reagents, a range of ethyl cellulose ethers may be obtained of various degrees of etherification and showing a great range of solubility, some of them being soluble in cold water but coagulated on heating.

H. Dreyfus[1] prepares alkyl ethers of cellulose by steeping cellulose in a solution of caustic soda or potash sufficiently dilute to permit of the uniform distribution of 2-4 molecules of alkali per molecule of cellulose. The water is then more or less completely removed by evaporation *in vacuo*, preferably under a very high vacuum. The mass of alkali cellulose is treated with methyl or ethyl sulphate or chloride, which may be employed alone or diluted with a neutral solvent such as benzene to ensure uniform distribution, at a temperature preferably not exceeding 50°-60°. The solubility of the

1. F.P. 462274, 1912; abst. J.S.C.I. 1914, 33, 248.

products may be modified by subsequent treatment with mineral or organic acids, the action being interrupted at any stage when the desired solubility is attained.

For the manufacture of artificial filaments,[1] the cellulose ethers, placed in solution by means of ethyl ether or benzene or both, are mixed with coloring matters and pigments, either with or without the addition of nitrated or acetylated cellulose, and forced into fine threads in the usual manner.

W. Denham and H. Woodhouse[2] have methylated cellulose by the action of methyl sulfate on the fibrous substance, "madder bleached calico" wet beaten to a fine pulp and then dried, and cotton wool being used in the experiments. The cellulose was converted into alkali-cellulose by treatment with rather more than 2 molecules of sodium hydroxide and was then treated with a considerable excess of methyl sulfate. The product was washed successively with water, very dilute alkali and acid, and then again with water. Its composition corresponded with the formula $C_{12}H_{19}O_9.OCH_3$. On subjecting it to a second methylation in a similar manner, a product of the formula, $C_6H_9O_4.OCH_3$, was obtained, and a third methylation yielded a product of the composition, $C_{24}H_{35}O_{15}(OCH_3)_5$. The methylated celluloses are fibrous, but become more and more horny in appearance with increasing degree of methylation. The first product dissolves readily, the others less easily, in cuprammonium solution, and only the first appears to be soluble in a solution of zinc chloride in hydrochloric acid. They can all be acetylated, the acetyl derivatives being soluble in chloroform and bearing some resemblance to acetylcelluloses; they contain less carbon, hydrogen and methoxyl than would correspond to completely acetylated derivatives of the methylated celluloses. The product, $C_6H_9O_4.OCH_3$, can be converted into a xanthate by means of methylated cellulose regenerated from the filtered solution of sodium hydroxide solution and carbon bisulphide. The

1. L. Lilienfeld, E.P. 6387, 1913; abst. Kunst. 1914, 4, 236. For preparation of cellulose in concentrated HCl, see R. Willstaetter, DRP 273800; abst. Kunst. 1914, 4, 179.

2. J.C.S. 1913, 103, 1735; abst. Jour. Dyers Col. 1913, 29, 327; JSCI 1913, 32, 974; Chem. Zentr. 1913, II, 1857.

the xanthate contains slightly less methoxyl than the original substance. Starch can be methylated in a similar manner. This field, which is comparatively new, offers many industrial possibilities, especially in the formaton of artficial filaments and difficultly flammable plastics.

Acetolysis and Octa-Acetylcellobiose. Decomposition of cellulose to cellobiose first caused by Skraup and his pupils by means of acetic acid anhydride in the presence of sulfuric acid is the process called acetolysis, and is of especial importance in this connection because as a result of the investigations in this direction, much has been revealed as to the mechanism of the process of acetylation and hydrolysis.

Z. Skraup [1], in repeating the work of Franchimont, found that when cellulose is treated with sulfuric acid and acetic acid anhydride, if low temperatures and small quantities of sulfuric acid are used, the products are more complicated than when these precautions are not observed. What was at first considered to be a pentacetylhexose was afterwards[2] shown to be a cellobiose octacetate, of crystalline structure, and melting at 227-228°, and yielding upon saponification a biose, cellobiose. By the action of hydrochloric acid on the acetyl derivative, an acetochloro compound results, from which, by replacing the chlorine by acetyl, a new acetyl compound was obtained of m. pt. 200°, isomeric with the product mentioned above. A hepta-acetylchlorocellobiose, formed by the action of HCl on heptacetylcellobiose, melted at 178°.[3] L. Macquenne and W. Goodwin[4], preparing cellobiose by a modification of Skraup's process, obtained two octacetyl derivatives,

1. Ber. 1899, **32**, 2413; abst. J.C.S. 1899, **76**, 852; Jahr. Chem. 1899, 1288; JSCI 1899, **18**, 941; Chem. Centr, 1899, **70** [(5)**3**,] II, 752; Bull. Soc. Chem. 1900, (3) **24**, 619.

2. Z. Skraup and J. Koenig, Ber. 1901, **34**, 1115; J.S.C.I. 1901, **20**, 740; J.C.S. 1901, **80**, i, 370; Jahr. Chem. 1901, 878; Chem. Centr. 1901, I, 1197.

3. Z. Skraup and J. Koenig, Monatsh. 1901, **22**, 1011; abst. Centr. 1902, **75**, 183; J.S.C.I. 1902, **21**, 144. For acetochlorglucose JCS 1902, **82**, i, 135; Bull. Soc. Chim. 1902, (3) **28**, 927; Chem. and acetochlorgalactose, see Z. Skraup and R. Kremann, Monatsh. 1901, **22**, 1037; abst. J.S.C.I. 1902, **21**, 144; Bull. Soc. Chim. 1902, (3), **28**, 928. Monatsh. 1902, **22**, 375; abst. Bull. Soc. Chim. 1902, (3), **28**, 482; J.S.C.I. 1901, **20**, 513.

4. Bull. Soc. Chim. 1904, (3), **31**, 854; abst. J.C.S. 1904, **86**, i, 799; Chem. Centr. 1904, II, 645; Jahr. Chem. 1904, I, 1149.

one melting at 228-229° and the other melting at 196° and instantly converted into the first form by heating with acetic anhydride and sulfuric acid. Skraup [1] subsequently prepared the acetochloro derivative directly from cellulose, but was unable to obtain a biose from the acetyl modification with melting point of 200°. E. V. Hardt-Stremayr [2] found that the acetates of Macquenne and Goodwin and of Skraup are identical, the true melting point being 196°.

In the method of F. Klein,[3] for the preparation of cellobiose octacetate, 10 grms. of cellulose are treated with 50 grms. of a mixture containing 80% of acetic anhydride and 20% of sulphuric acid, with special precautions to avoid local rise of temperature in the early stages. Subsequently the temperature may be raised to 35° or even 60° in order to accelerate the action. After 2-4 days the liquid sets to a mass of crystals; it is then diluted with glacial acetic acid and poured into a litre of water. The dried precipitate is recrystallized from three times its weight of 96% alcohol, the crystals forming long needles or leaflets. With proportions less than 3.5% of sulphuric acid or more than 30%, no crystallization of the octacetate is obtained. Hydrocellulose gives the same result as cellulose and is more easily manipulated. The highest yield of cellobiose octacetate obtained is 60% of the weight of cellulose, or about 30% of the theoretical quantity. Although not more than about one-third of the monose groups of cellulose are obtained in the form of cellobiose octacetate, the evidence is quite in accordance with the view that all these groups are combined in the same manner. The by-products are of two kinds: acetylated cellulosedextrins and products soluble in water of the nature of mixed aceto-sulphuric esters. The acetates obtained from the alcoholic

1. Monatsh. 1905, **26**, 1415; abst. J.C.S. 1906, **90**, i, 67; Jahr. Chem. 1905-08, II, 929.

2. Wien. Akad. Ber. **116**, 2-b, 3; Monatsh. 1907, **28**, 63; abst. JCS 1907, **92**, i, 389; Chem. Zentr. 1907, I, 1570; JSCI 1907, **26**, 482; Bull. Soc. Chim. 1908, (4), **4**, 4; Jahr. Chem. 1905-8, II, 922; C.A. 1907, **1**, 2179. See also Hardt-Stremayr, Wien. Akad. Ber. **116**, II-b, 13; abst. Jahr. Chem. 1905-8, II, 922.

3. Zts. ang. Chem. 1912, **25**, 1409; abst. J.S.C.I. 1912, **31**, 713; Chem. Zentr. 1912, **83**, 1196; Chem. Tech. Rep. 1912, **36**, 532; Kunst. 1912, **2**, 311; C.A. 1913, **6**, 2303.

mother-liquors from the crystallization of the cellobiose octacetate, having specific rotations from +11° to +34°, are doubtless intermediate products of the break-down of the cellulose molecule. The regular rise in the rotary power and percentage of combined acetic acid, in these fractionated dextrin acetates, makes it almost certain that acetolysis proceeds in a regular series of steps. The products soluble in the aqueous liquors after precipitating the dextrin and cellobiose acetates have not been fully investigated; in certain circumstances, these water-soluble products amount to 40% of the weight of the cellulose, and their properties suggest that they are probably aceto-sulphates either of cellobiose or of dextrose. The experimental methods of investigating the various products of acetolysis include observations of melting point, hygroscopic moisture, specific rotatory power in chloroform solution, combined acetic acid, cupric reducing power and solubility of the free dextrins obtained on saponification. The combined acetic acid is best determined by hydrolysis with a mixture of equal volumes of sulphuric acid and water and titration of the volatile acid. Alkaline saponification with *N*/2 alcoholic sodium hydroxide for 12-18 hours must be resorted to when it is desired to investigate the free dextrins; the acetic acid thus found is 1-3% higher than by acid hydrolysis. For the isolation of the free dextrins soluble in water, saponification with baryta water is more convenient. The melting points of the dextrin acetates are very doubtful and range round about 100°; cellobiose octacetate alone melts sharply, at 222°; the combined acetic acid is 70.4%, and $[a]_D = +41.7°$.

H. Ost and T. Katayama[1] acetylated cellulose, hydrocellulose, and alkali-cellulose both in presence of zinc chloride and of sulphuric acid, under similar conditions, and the resulting acetates were examined as regards solubility in alcohol, acetone, and chloroform, and the dissolved fractions tested for rotatory power and acetic acid content. In the first series

1. Zts. ang. Chem. 1912, **25**, 1467; abst. J.S.C.I. 1912, **31**, 713; Jour. Ind. Eng. Chem. 1912, **4**, 701; Kunst. 1912, **2**, 311; Chem. Tech. Rep. 1912, **36**, 485; Wagn. Jahr. 1912, II, 560; C.A. 1913, **6**, 2303; Chem. Zentr. 1912, II, 1199.

of experiments, 5 grms. of the cellulose was acetylated at 70° with 25 grms. of acetic acid, 25 grms. of acetic anhydride, and 2.5 grms. of zinc chloride; the acetates obtained from hydro-cellulose and alkali-cellulose, after like periods, contained larger percentages soluble in acetone than the acetates of cellulose; in each case the percentage soluble in acetone increased with the period of acetylation, indicating hydrolysis. Both hydro-cellulose and alkali-cellulose were completely esterified within two hours, whilst the cellulose required 20 hours. After 65 hours treatment, the acetates from cellulose contained 21.7 and 22.5% soluble in acetone, whilst after 2 hours the esters from hydro-cellulose contained 18.9% and after 20 hours 32.8%, and those from alkali-cellulose after 2 hours' treatment 27.1% soluble in acetone. These acetone-soluble portions gave films which were either very brittle or non-elastic. In the second series of experiments the same quantities were used, but the zinc chloride was replaced by 0.5 grm. of sulphuric acid and acetylation was carried out at the ordinary temperature; in these experiments only cellulose and hydro-cellulose were used, and the ester mixtures from these appeared identical after 48 hours; the percentages soluble in acetone were 20.0 and 24.8, respectively. The specific rotatory power of the fractions soluble in chloroform from cellulose and hydro-cellulose varied between —20.5° and —21.1°, and from alkali-cellulose from —21° to —22°; the figures for the corresponding portions soluble in acetone were —17.3 to —17.8°, and —21.8°. The acetic acid content of the chloroform- and acetone-soluble fractions agreed in all cases with that of cellulose triacetate, except that of cellulose acetylated in presence of zinc chloride for 65 hours, when it was slightly higher. In the third series of experiments, cellulose and hydro-cellulose were acetylated in presence of sulphuric acid at 70°; in this case more than half the product was soluble in alcohol, and the remainder completely soluble in acetone; when 1 grm. of sulphuric acid was used instead of 0.5 grm., the products were almost completely soluble in alcohol, and consisted principally of cellobiose-octa-acetate;

under suitable conditions this ester is converted into *a*-dextrose-penta-acetate, of m. pt. 112°.

E. Knoevenagel[1] has shown that acetolysis occurs in the presence of many contact substances besides sulfuric acid, in the presence of acetic anhydride, and has intimately studied the effect of acetic anhydride upon benzolacetone in the presence of ferric chloride.

G. Zemplen[2] found that when cellulose and hydro-cellulose are subjected to acetolysis preferably under the conditions described by Klein, both yield practically the same amount (50-55%) of cellobiose octacetate. According to his results, amyloid is not identical with hydro-cellulose, and hydrolysis by 70% sulfuric acid, even after prolonged action does not extend to the cellobiose groups, for the final product yielded no dextrose pentacetate as the result of the acetolysis.

H. Ost[3] found by the action of dilute sulphuric acid upon cellulose, that hydro-cellulose is very readily formed, but not more than about one-half of the cellulose can be made to undergo total hydrolysis to dextrose by this means. Moreover, there appear to be no intermediate products (dextrins) between hydro-cellulose and dextrose when cellulose is hydrolysed by dilute acids. According to the author's experiments, neither cellulose nor hydro-cellulose become perfectly anhydrous when dried at 100°-105°; the sample should be heated slowly up to that temperature and finally dehydrated at 120°-125°. Between that temperature and 130° or even 140°, purified cotton cellulose remains white and suffers no further loss of weight, but certain samples of hydro-cellulose are slightly decomposed by heating at 125°-130°.

1. Zts. ang. Chem. 1909, **22**, 281; abst. Chem. Ztg. 1909, **31**, 104. See also "Dissertation on the Hydrolytic and Acetolytic Breaking up of Cellulose under the Influence of Different Contact Substances," Heidelberg, 1911. W. Schleimann, "Cellobiose and the Acetolysis of Cellulose," Zts. ang. Chem. 1912, **25**, 771; Ann. 1911, **378**, 366; abst. Bull. Soc. Chim. 1911, (4), **10**, 1346; C.A. 1911, **5**, 1276; Chem Zentr. 1911, I, 807; J.S.C.I. 1911, **30**, 126.

2. Zts. physiol. Chem. 1913, **85**, 180; abst. J.S.C.I. 1913, **32**, 651; J.C.S. 1913, **104**, i, 708; C.A. 1913, **7**, 3836; Chem. Zentr. 1913, II, 426.

3. Ann. 1913, **398**, 313; abst. J.S.C.I. 1913, **32**, 784; Kunst. 1913, **3**, 352; C.A. 1913, **6**, 3836; J.C.S. 1913, **104**, i, 446, 833, 1148; Chem. Zentr. 1913, II, 2035; Ber. 1913, **46**, 2995. See also Ost, Zts. ang. Chem. 1912, **25**, 1996; abst. Kunst. 1913, **3**, 330.

Hydro-cellulose is less hygroscopic than cellulose. When both substances are corrected for the hygroscopic moisture expelled at 120°, elementary analysis fails to show any difference between cellulose and hydro-cellulose. The quantity of water combining with the cellulose in this first stage of hydrolysis falls within the limits of analytical error. When cellulose is hydrolysed by means of strong sulfuric acid, it forms the acid esters of a series of cellulose dextrins, which by heating at 120°, after dilution, may be almost quantitatively resolved into dextrose. Any "amyloid" precipitated by dilution must again be treated with strong sulphuric acid before it can be completely hydrolysed. Sulphuric acid of 70% strength is a better reagent for the "sulpholysis" of cellulose than the more concentrated acid. When cellulose is acetylated by a mixture containing sulphuric acid as a catalyst, the solution on further standing, loses its viscosity and a range of dextrin acetates is produced, terminating in cellobiose octacetate and dextrose pentacetate. These hydrolysed products contain more combined acetic acid than cellulose triacetate. The author has investigated the most favorable conditions for the total acetolysis of cellulose to dextrose acetates. The best results are obtained with a mixture of equal parts of acetic anhydride and glacial acetic acid containing 10 grms. of sulphuric acid per 100 c.c. Cellulose is digested with about 11 times its weight of such a mixture at 18°-20° for 4-6 months. From the reaction-product a certain amount of cellobiose acetate crystallizes out; the liquid is poured into water and the dried precipitate is extracted with ether; the insoluble matter contains cellobiose acetate and the acetates of intermediate dextrins. The former separates on crystallization from 70% alcohol, while the dextrin acetates are precipitated from the mother liquors by water. The ethereal extract of the precipitate and the ethereal extract of the portion of the reaction product soluble in water contain the dextrose acetate; a portion of this crystallizes out as pentacetate and further quantities of pentacetate may be prepared by subsequent acetylation of the residual syrups with mixtures containing

only traces of sulphuric acid. Of crystallized products, cellobiose and dextrose acetates, 60.6% of the theoretical quantity have been obtained from cellulose, but the residual syrups containing acetates soluble in ether but not crystallisable, bring the total yield of simple products to over 92% of the theoretical. These residual syrups are identical with those obtained in the acetylation of dextrose, and the author concludes that the cellulose molecule is entirely composed of dextrose residues.

He claims[1] the total hydrolysis of cellulose to dextrose has only been accomplished by way of its esters. After conversion into the sulphuric ester, cellulose may be completely resolved, by "sulpholysis," by heating the solution with water at 120°, into its constituent hexose groups. In an analogous manner a similar resolution may be effected by "acetolysis" after conversion into the acetate. Hydrolysis of the cellulose complex must take place by the oxygen atoms, which unite the hexose residues by lactonic linkages, taking up each one molecule of water and forming two hydroxyl groups. Thus the $3mn$ hydroxyls of a cellulose molecule made up of mn dextrose residues will become on hydrolysis n $(3m+2)$ hydroxyls, and a dextrin which may be produced, composed for instance, of 10 dextrose residues, will contain, not 30, but 32 hydroxyls, whilst the biose will contain 4 and the monose 5 hydroxyls per C_6 unit. This progressive hydrolysis can only be detected by elementary analysis in its later stages, but it is more sharply indicated by the increase in the combined acetic acid in the esters. Thus cellulose triacetate contains 62.5% of acetic acid, the acetate of a dextrin, $C_{60}H_{102}O_{512}$ (with 32 hydroxyls) contains 64.4%, cellobioseoctacetate contains 70.8%, and dextrose pentacetate 76.9%. Cellulose may be converted into dextrose pentacetate in the following manner: 5 grms. of cellulose, 25 c.c. of acetic anhydride, 25 c.c. of acetic acid and 5.5 grms. of sulphuric acid are digested at 40°-45° for two days. The product is poured into water when it has reaced a stage when a minimum precipitation (biose-

1. Chem. Ztg. 1912, **36**, 1099; abst. J.S.C.I. 1912, **31**, 980; Kunst. 1912, **2**, 412; Jour. Soc. Dyers. 1912, **28**, 369.

acetate and humus matters) thereby results. The aqueous solution is exhausted with ether, which extracts a syrupy mixture of various acetates of dextrose. When this mixture is re-acetylated in the cold by acetic anhydride with only traces of sulphuric acid, a very large yield of pure dextrose-*a*-pentacetate, melting at 112°, is obtained.

Formic Acid occurs naturally in ants, certain caterpillars, pine needles and stinging nettles, but is usually manufactured by synthetical processes. Sodium formate may be prepared by the action of carbon monoxide upon an alkaline hydroxide in the presence of water,[1] the sodium formate being dissolved in a mixture of formic and sulfuric acids, and distilled.[2] The formate and acid are continuously run in reacting quantities into a converting chamber,[3] from which the acid is distilled off. The mixture of formic acid and sulfuric acid is preferably either cooled,[4] or distilled under reduced pressure[5] to prevent the destructive action of the mineral acid upon the

1. R. Koepp and Co. F.P. 342168, 1904; abst. J.S.C.I. 1904, **23**, 911; Mon. Sci. 1906, (4), **65**, 6. For method of preparing formates, see O. Dubosc, A. Luttringer and H. Denis, F.P. 421227, 1909.

2. M. Hamel, F.P. 341764, 1904; abst. J.S.C.I. 1904; **23**, 911; Mon. Sci. 1906, (4), **65**, 6. E.P. 7534, 1904; abst. J.S.C.I. 1905, **24**, 289, U.S.P. 806660, 1905; abst. J.S.C.I. 1906, **25**, 39; Mon. Sci. 1906, (4), **65**, 117.

3. H. Schroder, D.R.P. 234580, 1910; abst. J.S.C.I. 1911, **30**, 803; Chem. Zentr. 1911, I, 1767; Zts. ang. Chem. 1911, **24**, 1152; Chem. Tech. Rep. 1911, **35**, 314; Wagn. Jahr. 1911, **57**, II, 19; Chem. Ind. 1911, **34**, 321; C.A. 1911, **5**, 2922.

4. H. Howard, U.S.P. 960927, 1910; abst. J.S.C.I. 1910, **29**, 815; Mon. Sci. 1911, (5), **75**, 74; Chem. Tech. Rep. 1910, **34**, 403; C.A. 1911, **5**, 770.

In the process (F. Bayer & Co., F.P. 417815, 1909; abst. C.A. 1912, **6**, 1958) for the production of concentrated formic acid from formates, the formate is fed at 5-10°, into the calculated amount of sulfuric acid, which is vigorously stirred and cooled. At first only a partial conversion is effected, without decomposition of the formic acid. If the intimate mixture is heated very slightly the temperature rises without further application of external heat to 85°, the mass liquifies, but decomposition does not result. Upon distillation *in vacuo*, an almost theoretical yield is realized. With sulfuric acid of 63° Be. an 81% formic acid is obtained, and with sulfuric acid of 66° Be. a 91% formic acid is obtained. Only by using concentrated sulfuric acid is decomposition of formic acid observed.

5. Chem. Soc. Ind. Basle, E.P. 8438, 1910; abst. J.S.C.I. 1910, **29**, 1036; C.A. 1911, **5**, 2153; Chem. Tech. Rep. 1910, **34**, 482 D.R.P. 239075, 1910; abst. C.A. 1912, **6**, 2290; Zts. ang. Chem. 1911, **24**, 2132; Chem. Zentr. 1911, II, 1285; Wagn. Jahr. 1911, II, 20. F.P. 425321, 1911; abst. Mon. Sci. 1913, **78**, 119.

formic. The same result is also accomplished by either diluting the reaction mass with a hydrocarbon more volatile than formic acid as petroleum ether,[1] or by previously diluting the sulfuric acid with an aqueous liquid so that the heat of hydration may escape,[2] or by mixing with vitriol of not over 66° Be. strength, and maintaining a low temperature.[3] In the latter method, formic acid of at least 91% strength may be obtained by a single distillation. The sulfuric acid may be partially or wholly replaced by acid sodium sulfate,[4] sodium pyrosulfate,[5] or anhydrous copper sulfate;[6] or hydrofluoric,[7] oxalic,[8] or

1. H. Schroder, D.R.P. 245168, 1909; abst. J.S.C.I. 1912, **31**, 557; Zts. ang. Chem. 1912, **25**, 990; Chem. Tech. Rep. 1912, **36**, 295; Chem. Ind. 1912, **35**, 249; C.A. 1912, **6**, 2494; Chem. Zentr. 1912, I, 1266.

2. Soc. Anon. des Usines des Moulins, F.P. 382339, 1907; abst. J.S.C.I. 1908, **27**, 246; C.A. 1909, **3**, 2350; Mon. Sci. 1909, (4), **71**. 102; Chem. Tech. Rep. 1908, **32**, 178.

3. Farbwerke, vorm. Meister Lucius, und Bruning, E.P. 20893, 1909; abst. J.S.C.I. 1910, **29**, 1133; C.A. 1911, **5**, 2415. D.R.P 232707, 1908; abst. C.A. 1912, **6**, 1820; Chem. Tech. Rep. 1911, **35**. 211; Chem. Ind. 1911, **34**, 225. F.P. 417815, 1909; abst. J.S.C.I 1911, **30**, 27; Mon. Sci. 1913, **78**, 85; Chem. Tech. Rep. 1910, **34** 642. See also Nitritfabrik Copenick, D.R.P. 169730, 1903; 182691 1904; abst. C.A. 1907, **1**, 2061; Chem. Zentr. 1906, I, 1584; 1907, I 1469; Zts. ang. Chem. 1906, **19**, 1780; 1908, **21**, 216; Wagn. Jahr 1906, 14.

4. Chem. Fabr. Grunau, Landshoff und Meyer Akt-Ges. F.P. 367316, 1906; abst. J.S.C.I. 1906, **25**, 1173; Mon. Sci. 1908, (4), **69**. 73; E.P. 14438, 1906; abst. J.S.C.I. 1906, **25**, 1173; C.A. 1907, **1**. 940; U.S.P. 857046, 1907; abst. J.S.C.I. 1907, **26**, 839; C.A. 1907, **1**. 2504; D.R.P. 193509, 1905; abst. J.C.S. 1908, **94**, i, 598; Chem Zentr. 1908, I, 998; Zts. ang. Chem. 1908, **21**, 1090; Jahr. Chem 1905-08, II, 343; Chem. Zts. 1908, **7**, 562; Wagn. Jahr. 1905, **54**, II 11; Chem. Ind. 1908, **31**, 102.

5. A. Hempel, E.P. 3428, 1908; abst. J.S.C.I. 1909, **28**, 259; C.A. 1909, **3**, 2207; Chem. Tech. Rep. 1909, **33**, 334; F.P. 389039 1908; U.S.P. 1017261, 1912; abst. J.S.C.I. 1908, **27**, 958; 1912, **31**. 282.

6. Chem. Fabr. Griesheim-Elektron, D.R.P. 230171, 1909; abst. J.S.C.I. 1911, **30**, 360; C.A. 1911, **5**, 2536; Zts. ang. Chem 1911, **24**, 286; Chem. Zentr. 1911, **82**, 359; Chem. Tech. Rep. 1911. **35**, 79; Wagn. Jahr. 1911, II, 21; Chem. Ind. 1911, **34**, 82. For the use of sulfonic acids, see also their D.R.P. 235752, 1909; abst C.A. 1911, **5**, 3488; 1912, **6**, 960; Zts. ang. Chem. 1911. **24**, 1549; Chem. Zentr. 1911, **82**, 240; Chem. Tech. Rep. 1911, **35**, 348; Chem Ind. 1911, **34**, 428.

7. D. Strauss, D.R.P. 209418, 1907; abst. J.S.C.I. 1909, **28**, 674; C.A. 1909, **3**, 2211; Zts. ang. Chem. 1909, **22**, 1082; Chem Zentr. 1909, **80**, 1915; Chem. Zts. 1909, **8**, 1507; Chem. Tech. Rep 1909, **33**, 209; Wagn. Jahr. 1909, **55**, II, 19; Chem. Ind. 1909, **32**, 311. For the method of O. and P. Piequet, see Belg. P. 185701

phosphoric acids.[1] Ammonium formate[2] is claimed to have certain advantages over the sodium salt as the source for formic acid. To produce a more uniform combination, a gas indifferent to the reaction mixture may be caused to circulate from the still through the condenser and into the receiver, and thence back to the still, carrying the vapor of formic acid from the former into the latter.[3]

In the hydrolysis of alkaline earth cyanides for the preparation of ammonia,[4] formic acid is produced simultaneously. In a recently described process,[5] calcium cyanamide is converted into cyanide by heating with charcoal and a flux to lower the melting point of the mixture, and the latter transformed into ammonia and formic acid.[6] C. Kingzett and R. Woodcock[7] have described the production of formic

1905. Compare Electrochemische Werke, Belg. P. 188838, 1905.

8. Soc. Anon. des Etablissements Eycken et Leroy, F.P. 393 526, 1908; abst. J.S.C.I. 1909, **28**, 160; Mon. Sci. 1911, (4), **71**, 135; Chem. Tech. Rep. 1909, **83**, 53.

1. H. Howard U.S.P. 970825, 975866, 1910; abst. Mon. Sci. 1911, (5), **75**, 98; Chem. Tech. Rep. 1911, **85**, 86; J.S.C.I. 1910, **29**, 815, 1453; C.A. 1910, **4**, 3286; 1911, **5**, 770. M. Neumann, U.S.P 975151, 1910; abst. J.S.C.I. 1910, **29**, 1453; C.A. 1911, **5**, 770. W. Walker, U.S.P. 970145, 1910; abst. C.A. 1910, **4**, 3286.

2. Chem. Fabr. Grunau, Landshoff, Meyer, E. Franke and W. Kirchner, D.R.P. 243225, 1910; abst. J.S.C.I. 1912, **31**, 334; Chem. Zentr. 1912, **83**, 618; Zts. ang. Chem. 1912, **25**, 508; Chem. Tech Rep. 1912, **36**, 159; Chem. Ind. 1912, **35**, 152; C.A. 1912, **6**, 2292. In the process of the Soc. pour L'Industrie Chim. Bale, (F.P. 425321 1910; abst. J.S.C.I. 1911, **30**, 1012) a formate is heated with concentrated sulfuric acid in the presence of pure, concentrated formic acid, it being found that when the latter is in excess, it is not affected by sulfuric acid. After the reaction, the formic acid is distilled off preferably under diminished pressure.

3. J. Weise, U.S.P. 1043985, 1912; abst. J.S.C.I. 1912, **31**, 1178.

4. Badische Anilin and Soda Fabr. F.P. 372714, 1906; abst. J.S.C.I. 1907, **26**, 527; Mon. Sci. 1908, (4), **69**, 82. E.P. 22038, 1906; abst. J.S.C.I. 1907, **26**, 967.

5. H. Sulzer, Zts. ang. Chem. 1912, **25**, 1268; abst. J.S.C.I. 1912, **31**, 682; Chem. Zentr. 1912, I, 814; J.C.S. 1912, **102**, i. 610; Chem. Tech. Rep. 1912, **36**, 405.

6. H. Sulzer-Rieter, D.R.P. 243797, 1911; abst. J.S.C.I. 1912, **31**, 385; Zts. ang. Chem. 1912, **25**, 605; Chem. Zentr. 1912, II, 761; Chem. Tech. Rep. 1912, **36**, 146; Chem. Ind. 1912, **35**, 190; Wagn Jahr. 1912, II, 29. E.P. 784, 1912; abst. J.S.C.I. 1912, **31**, 817. F.P. 438965, 1912; abst. J.S.C.I. 1912, **31**, 588; Mon. Sci. 1913, **78**, 136.

7. J.S.C.I. 1912, **31**, 265; Chem. Zentr. 1912, I, 1715; Zts. ang. Chem. 1912, **25**, 1657; J.C.S. 1912, **102**, i, 367; Chem. News 1912,

and acetic acids by the atmospheric oxidation of turpentine,[1] while M. von Unruh[2] has patented a process for obtaining formic acid by the oxidation of methyl alcohol.

Anhydrous formic acid prepared from sodium formate is liable to contain traces of sulfur and chlorine.[3] These may be removed by shaking with litharge for 24 hours, redistilling and then precipitating the sulfur by dilution, sulfur being insoluble in 25% acid. Absolute formic acid may be prepared by repeated distillation over anhydrous copper sulfate under diminished pressure.[4] Formic acid melts at 8.35°, boils at 99.7° at 741 mm. pressure. The density is 1.2322 at 10°, 1.226 at 15°, 1.22 at 20°, 1.2139 at 25°, 1.2078 at 30°, 1.2019 at 25°, and 1.1957 at 40°.[5] It is miscible with water, alcohol, and acetic acid in all proportions. Formic acid is an excellent solvent for acetated cellulose, for which purpose it has been patented,[6] and is a direct partial solvent of cellulose with the

105, 26; Chem. Tech. Rep. 1912, 36, 360; C.A. 1912, 6, 1275.

1. For the catalytic esterification of formic acid, see P. Sabatier and A. Mailhe, Compt. Rend., 1911, 152, 1044; abst. J.S.C.I. 1911, 30, 648; Bull. Soc. Chim. 1912, (4), 11, 84; J.C.S. 1911, 100, i, 416; C.A. 1911, 5, 2630; Chem. Zentr. 1911, I, 1810. For exhaustive article on the manufacture of formic acid, see A. Dubosc Bull. Soc. Chim. (Rouen), 1907, 38, 128-89, 328-63; 1913, 41, 83-6; abst. C.A. 1911, 5, 473; 1913, 7, 504. O. Dubosc, A. Luttringer and H. Denis, U.S.P. 1019230, 1912. For the properties of formic acid, see T. Walther, Faerb. Ztg. 1911, 22, 61, 83; abst. J.S.C.I. 1911, 30, 416.

2. U.S.P. 891753, 1907; abst. J.S.C.I. 1908, 27, 918; Chem. Tech. Rep. 1908, 32, 413. For the A. Hempel method of producing formates, see F.P. 389039, 1908; U.S.P. 1017261, 1912; abst. J.S.C.I. 1908, 27, 958; 1912, 31, 282. See also J. E. Bucher, U.S.P. 1083589, 1914; abst. C.A. 1914, 7, 991.

3. E. Rupp, Arch. Pharm. 1905, 243, 69; abst. J.S.C.I. 1905, 24, 353; J.C.S. 1906, 90, ii, 907; Chem. Zentr. 1905, I, 962; Jahr. Chem. 1905-8, II, 345; J.C.S. 1905, 88, ii, 291; Zts. ang. Chem. 1905, 18, 1271.

4. J. Garner, B. Saxton, H. Parker, Amer. Chem. J. 1911, 46, 236; abst. J.S.C.I. 1911, 30, 1185; C.A. 1911. 5, 3681; J.C.S. 1911, 100, i, 831; Bull. Soc. Chim. 1912, (4), 12, 208; Chem. Zentr. 1912, I, 122.

5. For other determinations of pure formic acid, see O. Pettersson, J. pr. Chem. 1881, 24, 296; abst. Jahr. Chem. 1881, 1096; J.C.S. 1882, 42, 3. K. Hartwig. J.C.S. 1891, 60, 1308; abst. Jahr. Chem. 1891, 280. V. Sapojnikoff, J. Russ, Phys. Chem. S. 1894, 25, 109; abst. J.C.S. 1894, 66, 66. Zanninovich-Tessarin, Zts. Phys. Chem. 1896, 19, 251; abst. J.C.S. 1896, 70, ii, 352; Chem. Zentr. 1896, I, 733; Jahr. Chem. 1896, 112; Bull. Soc. Chim. 1896, (3), 16, 1330.

6. U.S.P. 922340, 1909; abst. J.S.C.I. 1909, 28, 671. F.P.

formation at the same time of esters. Formic acid solutions of cellulose formate have been advocated for the manufacture of artificial silk,[1] as a solvent for starch,[2] and as a constituent in compound solvent combinations. In the formylation of cellulose and starch, it is necessary, for best results, that acid of at least 98% concentration be employed, and that the acid be substantially free from impurities. In handling concentrated formic acid, it should be remembered that serious burns result from contact of the acid with the skin, even in the cold.

Acetic Acid occurs in nature in many plants, usually as the potassium or calcium salt, and in the form of esters in many seed essential oils. Being an unusually stable body at a wide range of temperatures, it is found as a product of decomposition in destructive distillation of many organic substances, especially wood, from which the major portion of the acetic acid of commerce is obtained.

Acetic acid may be obtained by distilling calcium acetate with sulfuric acid[3] under reduced pressure,[4] the distillation of the acetic acid being facilitated in the presence of an immiscible volatile liquid, such as xylol.[5] Calcium acetate may also

400652, 1909; abst. J.S.C.I. 1909, **28**, 1061; Mon. Sci. 1910, (4), **73**, 165. D.R.P. 237718, 1907; abst. Zts. ang. Chem. 1911, **24**, 1988; Chem. Zentr. 1911, **82**, [(5), **15**], II, 922; Chem. Ind. 1911, **34**, 573; Chem. Tech. Rep. 1911, **35**, 481. It. P. 303-136-101262, 1909.

1. E.P. 3973, 1911; abst. J.S.C.I. 1911, **30**, 1143, 1156; C.A. 1912, **6**, 2172. F.P. 426436, 1911; abst. J.S.C.I. 1911, **30**, 950. Aust. P. Appl. A. 327-11, Jan. 12, 1911. Belg. P. 232475, 1911.

2. D.R.P. 137330, 1901; abst. Chem. Centr. 1903, **74**, 7, 306; Jahr. Chem. 1903, 1005; Zts. ang. Chem. 1903, 16, 90. F.P. 322206, 1902; abst. J.S.C.I. 1903, 22, 310. E.P. 10872, 1902; abst. J.S.C.I. 1903, 22, 642. U.S.P. 778173, 1904; abst. J.S.C.I. 1905, **24**, 98. E.P. 9868, 1902; abst. J.S.C.I. 1903, **22**, 1008; Mon. Sci. 1904, (4), **60**, 37. F.P. 334154, 1903; abst. J.S.C.I. 1904, **23**, 29. D.R.P. 182558, 1903; abst. Zts. ang. Chem. 1907, **20**, 179; Mon. Sci. 1909, **70**, 77. Belg. P. 171743, 1903.

3. F. Bayer & Co., D.R.P. 220705, 1907; abst. J.S.C.I. 1910, **29**, 564; Zts. ang. Chem. 1910, **23**, 1092; Chem. Zentr. 1910, I, 1470; Chem. Tech. Rep. 1910, **34**, 215; Chem. Ind. 1910, **33**, 302; Wagn. Jahr. 1910, II. 7; Chem. Zts. 1910, **9**, 1974.

4. J. Behrens, F.P. 386734, 1908; abst. J.S.C.I. 1908, **27**, 749; Mon. Sci. 1909, **71**, 108; C.A. 1909, **3**, 2360.

5. L. Marckwald, D.R.P. 172931, 1904; abst. J.S.C.I. 1907, **26**, 312; Zts. ang. Chem. 1907, **20**, 365; Chem. Zentr. 1906, II, 834; Wagn. Jahr. 1907, 16; Jahr. Chem. 1905-8, 349.

be dissolved in concentrated acetic acid previously saturated with sulfurous acid, the calcium sulfite produced being separated by filtration, and the acetic acid contained therein recovered by distillation.[1] Sulfuric acid may be substituted by hydrochloric acid.[2] In the M. Mugdan process,[3] silicon tetrachloride is caused to react upon a metallic acetate as sodium acetate at normal pressure and a temperature of 100-180°, the acetic acid being distilled off.

Several methods of obtaining acetic acid from sawdust have been described, as by treatment with mineral acid and passage of the vapors through a red hot tube,[4] an after treatment for removal of formic acids being required,[5] but, as yet, these processes may be said to be but in the experimental stage. The intermediate product is ethyl alcohol. Behrens first oxidizes the alcohol to aldehyde[6] in the presence of air and a platinum contact, the aldehyde being separated by fractional distillation, rendered conductive by the addition of water and sulfuric acid, and oxidized electrolytically to acetic acid. Vanadium pentoxide[7] is also claimed as an efficient catalyst.

1. A. Behrens, E.P. 22096, 1902; abst. J.S.C.I. 1903, **22**, 110. For the M. Prager continuous process, see E.P. 24327, 1912; F.P. 449622, 1912; D.R.P. 260232, 1912; abst. J.S.C.I. 1913, **32**, 486,868; C.A. 1913, **7**, 3206; 1914, **8**, 1344; Zts. ang. Chem. 1913, **26**, 400; Chem. Zentr. 1913, II, 103. For the manufacture of acetic acid by the destructive distillation of coffee husks, see G. Calvert, E.P. 10687, 1913; abst. J.S.C.I. 1914, **33**, 636. See F. Villani, L'Ind. Chimica, 1909, **9**, 365; abst. J.S.C.I. 1909, **28**, 169. H. Ost and F. Klein, Chem. Ztg. 1908, **32**, 815.

2. P. Boessneck, U.S.P. 715748, 1902; abst. J.S.C.I. 1903, **22**, 110. H. von Hochstetter, E.P. 3923, 1902; abst. J.S.C.I. 1903, **22**, 378. F.P. 318710, 1902; abst. J.S.C.I. 1902, **21**, 1469; Mon. Sci. 1903, (4), **59**, 121; U.S.P. 714484, 1906; abst. Mon. Sci. 1903, (4), **59**, 77. U.S.P. 944372, 1909; abst. C.A. 1910, **4**, 643; Mon. Sci. 1910, (4), **73**, 89.

3. U.S.P. 944372, 1909; abst. C.A. 1910, **4**, 643.

4. J. and A. Mueller, F.P. 357432, 1905; abst. J.S.C.I. 1906, **25**, 117.

5. Comp. Industrielle des Alcools de l'Ardeche, F.P. 404360, 1908; E.P. 18028, 1909; abst. J.S.C.I. 1910, **29**, 211, 646.

6. D.R.P. 223208, 1908; abst. J.S.C.I. 1910, **29**, 948; Zts. ang. Chem. 1910, **23**, 1584; Chem. Zentr. 1910, II, 347; Chem. Tech. Rep. 1910, **34**, 392; Chem. Ind. 1909, **33**, 459; Wagn. Jahr. 1910, II, 6; C.A. 1910, **4**, 2987. For the electrolytic oxidation of ethyl alcohol to acetic acid, see P. Askenasy, R. Leiser and N. Gruenstein; Zts. Elektrochem, 1909, **15**, 846; abst. J.S.C.I. 1909, **28**, 1266; J.C.S. 1909, **i**, 869.

7. Chem. Fabr. Griesheim Elektron, E.P. 17424, 1911; 8076,

In the preparation of acetic acid from ethylene [1] or acetylene,[2] aldehyde [3] is oxidized directly to acetic acid.

Acetic acid may be purified by distillation with potassium permanganate,[4] using a still head to retain acids of higher boiling point; by distillation with phosphoric acid,[5] or by slow distillation of sodium bisulfate with a non-volatile mineral acid.[6] In the J. Behren's process,[7] the crude acid is

1912; abst. J.S.C.I. 1912, **31**, 772; 1913, **32**, 141; C.A. 1913, **7**, 399. U.S.P. 1081959, 1913; abst. Mon. Sci. 1914, **80**, 66; J.S.C.I. 1914, **33**, 77; C.A. 1914, **8**, 787. F.P. 440658, 1912; abst. J.S.C.I. 1912, **31**, 817. D.R.P. 261589, 1911; abst. J.C.S. 1913, **104**, i, 1041; C. A. 1913, **7**, 3641; Can. P. 143330, 1912; abst. C.A. 1913, **6**, 400. Swiss P. 62720, 1912; abst. C.A. 1914, **8**, 2249. See C.A. 1912, **6**, 3496.

1. Cie Urbaine d'Eclairage par le Gaz Acetylene F.P. 338965, 1903; abst. J.S.C.I. 1904, **23**, 1043. E. L. Rinman, D.R.P. 244816, 1911; abst. J.S.C.I. 1912, **31**, 532; Zts. ang. Chem. 1912, **25**, 1035; Chem. Tech. Rep. 1912, **36**, 249; Wagn. Jahr. 1912, II, 553; Chem. Zentr. 1912, I, 107. E. French, D.R.P. 249333, 1911; abst. J.S.C.I. 1912, **31**, 914; Zts. ang. Chem. 1912, **25**, 1886; Chem. Zentr. 1912, II, 465; Chem. Tech. Rep. 1912, **36**, 468; C.A. 1912, **6**, 3181; Wagn. Jahr, 1912, **58**, 31.

2. L. Deglatign and M. Jouas, M. Desmonts, and L. Dubosc, F.P. 360180, 360249, 1905; abst. J.S.C.I. 1906, **25**, 496.

3. C. Kingzett, J.C.S. 1874, **27**, 511; Chem. Centr. 1874, 566; Jahr. Chem. 1874, 188; J.C.S. 1875, **28**, 210; Chem. Centr. 1875, 422; Mon. Sci. (3), **5**, 1020; Jahr. Chem. 1875, 156; J.C.S. 1880, **37**, 792; Jahr. Chem. 1880, 248; C.N. 1880, **41**, 254; Chem. Centr. 1881, 473; J.C.S. 1884, **45**, 93; Jahr. Chem. 1884, 1272; Chem. Centr. 1884, 327; Chem. News, **32**, 138; **34**, 127; **39**, 279; J.S.C.I. 1886, **5**, 7; 1888, **7**, 549; 1890, **9**, 3; Chem. Trade Jour. **14**, 115; has studied the aerial oxidation of the terpenes.

4. W. Bousfield and T. Lowry, Proc. Chem. Soc. 1911, **27**, 187; J.C.S. 1911, 1432; Chem. Zentr. 1911, II, 852; Bull. Soc. Chim. 1912, (4), **12**, 149; abst. J.S.C.I. 1911, **30**, 891; C.A. 1911, **5**, 3568. According to the Consortium f. Elektrochem. Industrie (F.P. 460971, 1913; E.P. 17016, 1913; abst. J.S.C.I. 1914, **33**, 42, 422), the conversion of acetaldehyde into acetic acid by oxygen is accelerated by the addition of small quantities of manganese compounds; the reaction is not explosive, as is the case when compounds of chromium, vanadium, cerium, etc., are used as accelerators. Example: A current of dry oxygen is passed into a mixture of 300 kilos. of pure acetaldehyde and 2 kilos. of manganese acetate in a pure aluminum vessel provided with a stirrer and a cooling jacket; the manganese salt dissolves in the aldehyde, and the solution absorbs oxygen very energetically, the heat evolved being removed by external cooling. After 10 to 20 hours the absorption is complete and the acid is distilled. Air may be used in place of oxygen, and the gases may be introduced under pressure; acetic acid or other solvent may be added to the aldehyde, if desired.

5. K. Orton, M. Edwards, and H. King, Proc. Chem. Soc. 1911, **27**, 120; abst. J.S.C.I. 1911, **30**, 681; C.A. 1911, **5**, 3561; Chem. Zentr. 1911, II, 528.

6. G. v. Belotini, E.P. 20125, 1907; abst. J.S.C.I. 1907, **26**,

heated in a still, passed through a hot pipe mixed with air and a catalyst as platinized asbestos, manganic oxide, or finely divided copper, the temperature depending on the concentration of the final acid desired. Anhydrous copper sulfate has also been patented as a dehydrating agent in the manufacture of glacial acetic acid.[1] Scott and Henderson[2] purify the crude acetates by decolorizing with boiling sodium hypochlorite, cooling and crystallizing. Scott[3] directly distils the crude acid at 100°, and fractionally condenses the vapors.

Absolute acetic acid at ordinary room temperatures is a colorless strongly refracting liquid of density of 1.05148 at 18°/40°; 1.04922, 20°/40°;[4] 1.055, 18°/40°;[5] 1.055, 15°/4°; 0.9853, 76.5°/4°;[6] 1.0439, 25°/4°; 1.01561, 50°/4°;[7] 1.052.72, 17.5°/4°;[8] 1.0446, 22.9°/4°;[9] 1.0553, 15°/?; 1.0635, 15°/?, miscible

1291; see also G. Glock, E.P. 28595, 1902; abst. J.S.C.I. 1903, 22, 291.

7. E.P. 3392, 1901; abst. J.S.C.I. 1901, 20, 474. E.P. 28839, 1910; abst. J.S.C.I. 1911, 30, 746.

1. Chem. Fabr. Griesheim Elektron, D.R.P. 230171, 1909; abst. J.S.C.I. 1911, 30, 360; Zts. ang. Chem. 1911, 24, 286; Chem. Zentr. 1911, I, 359; Chem. Tech. Rep. 1911, 35, 79; Chem. Ind. 1911, 34, 83; Wagn. Jahr. 1911, II, 21; C.A. 1911, 5, 2536. For the resistance of sheet steel enamels to solution by acetic acid of various strengths, R. Landrum, Trans. Amer. Ceram. Soc. 1911, 13, 494; abst. J.S.C.I. 1911, 30, 1386; C.N. 1911, 103, 28; Chem. Zentr. 1911, I, 755; Chem. Eng., 12, No. 5.

2. E.P. 6711, 1896; see also Krauschwitzer Thonwaarenfabrik fur Chem. Ind. E.P. 25297, 1899; abst. J.S.C.I. 1901, 20, 42.

3. E.P. 12952, 1897.

4. R. Bousfield and T. Lowry, J.C.S. 1911, 99, 1439; abst. C. A. 1911, 5, 1432; Zts. ang. Chem. 1911, 24, 2084; Chem. Zentr. 1911, II, 852; Bull. Soc. Chim. 1912, (4), 12, 149. Their acetic acid fused within 0.005° of 16.60°.

5. D. Tsakalotos, Bull. Soc. Chim. 1911, (4), 9, 521; abst. C. A. 1911, 5, 3231; J.C.S. 1911, 100, i, 514; Chem. Zentr. 1911, II, 526.

6. K. Drucker and R. Kassel, Z. phys. Chem. 1911, 76, 369; abst. C.A. 1911, 5, 1859; J.C.S. 1911, 100, ii, 373; Chem. Zentr. 1911, I, 1395; Bull. Soc. Chim. 1911, (4), 10, 1473.

7. J. Hubbard. Z. phys. Chem. 1910, 74, 217; abst. C. A. 1910, 4, 2401; J.C.S. 1910, 98, ii, 809; Bull. Soc. Chim. 1911, (4), 10, 831; Chem. Zentr. 1910, II, 939.

8. V. Polowzow. Zts. phys. Chem. 1911, 75, 520; J.C.S. 1911, 100, ii, 101; Chem. Zentr. 1911, I, 609; Bull. Soc. Chim. 1911, (4), 10, 1205.

9. F. Eisenlohr, Zts. phys. Chem. 1911, 75, 585; abst. C.A. 1911, 5, 1218; J.C.S. 1911, 100, ii, 81; Chem. Zentr. 1911, I, 624; Bull. Soc. Chim. 1911, (4), 10, 1221. The following are recent density determinations compared with water at 4°: 20°=1.0502 (H. Malosse, Compt. rend. 1912, 154, 1697; abst. Chem. Zentr. 1912, II,

in all proportions without turbidity with water, methyl, ethyl, propyl, butyl and amyl alcohols, ethyl ether, acetone, chloroform, ethyl and amyl acetates, and, in general, a large number of organic compounds. Concentrated acetic acid is an excellent solvent of camphor, acetanilid, resorcinol diacetate, acetophenone, benzophenone and many other cellulose ester plastic-inducing bodies. Glacial acetic acid is usually understood to include an acid of 98% strength or higher, although the Pharmacopeas of the various countries vary greatly in the degrees of absoluteness required of official glacial acetic acid. Ability to mix with an equal volume of spirits of turpentine or oil of lemon are but approximate tests for freedom from water, but a 99% acetic acid will remain clear when mixed with two volumes of commercial lemon oil containing terpenes. The temperature of crystallization (16.632° a[1] is the most reliable approximate test of strength. Cellulose acetate

600; Bull. Soc. Chim. 1912, (4), 11, 309). 12.5°= 1.05819; 23.9° =1.04546; 30.4°=1.03797 (F. Schwers, J.C.S. 1912, 101, 1891; abst. Chem. Zentr. 1912, II, 2016; C.A. 1912, 6, 445, 562); 18.4°=1.05; 40°=1.034; 58.5°=1.012; 70°=0.999; 99°=0.964; C. Faust (Zts. phys. Chem. 1912, 79, 99; abst. Chem. Zentr. 1913, I, 382; Bull. Soc. Chim. 1912, (4), 12, 1092). When the number of gram equivalents of acetic acid are dissolved in 1000 c.c. of water, the following is the density at 25°, compared with water at the same temperature: 0.005 gm. equivalents of acetic acid equals density of 1.000048; 0.01, 1.000074; 0.02, 1.000182; 0.04, 1.000348; 0.1, 1.000873 (F. Cameron, J. Phys. Chem. 1910, 14, 571; abst. C.A. 1910, 4, 980, 2227; Chem. Zentr. 1910, II, 774). 0.5, 1.0026 (F. Usher, J.C.S. 1910, 97, 72; abst. C.A. 1910, 4, 1118; Chem. Zentr. 1910, I, 1007; Bull. Soc. Chim. 1911, (4), 10, 66). 0.093, 1.001; 0.1861, 1.0018; 0.3722, 1.0032; 0.6865, 1.0056; 0.7443, 1.0061; 0.9154, 1.0076; 1.373, 1.0112; 1.489, 1.0148; 2.746, 1.0217; 2.977, 1.0235 (A. Rivett and N. Sidgwick, J.C.S. 1910, 97, 735; abst. C.A. 1910, 4, 1833, 2900; Chem. Zentr. 1910, I, 2072; Bull. Soc. Chim. 1911, (4), 10, 522. E. Rimbach and R. Wintgen (Zts. phys. Chem. 1910, 74, 241; abst. C.A. 1910, 4, 2896; J.C.S. 1910, 98, ii, 810; Chem. Zentr. 1910, II, 939; Bull. Soc. Chim. 1911, (4), 10, 832) found 283.75 grms. acetic acid dissolved in 1000 c.c. solution gave sp. gr. 1.03235, 25°/4°.

1. E. Worden; unpublished results. The acetic acid employed was subjected to 165 crystallizations; starting with Merck's highest purity glacial, of approximately 99.85%. Other melting points recorded for acetic acid are: 16.75° (Petterson, J. pr. Chem. 1881, (2), 24, 296; abst. Ber. 1870, 3, 390; abst. Chem. Centr. 1870, 322, 578; 16.55° (F. Ruedorff. Jahr. Chem. 1870, 935; Bull. Soc. Chem. 1870, 14, 215; J.C.S. 1871, 24, 1093). 17.5° (E. Sonstadt, Chem. N. 1878, 37, 199; Jahr. Chem. 1878, 34). 16.4° (W. Ramsey and S. Young, J.C.S. 1886, 49, 805; abst. Chem. Centr. 1886, 643; Jahr. Chem. 1886, 233). 16.6713° (L. de Visser, Rec. trav. chim. 1893, 12, 115,

solutions in acetic acid have been advocated for photographic purposes,[1] and as a cellulose formate solvent.[2] The manufacture of artificial silk from acetylated cellulose in concentrated acetic acid[3] offers the advantage of forming solutions of great tenuity and clearness, the same being true of acetate lacquers in acetic acid for incandescent mantle impregnation.[4] In the preparation of soluble starch,[5] the esterification of

154; abst. Jahr. Chem. 1893, 277; Chem. Centr. 1893, II, 677; J.C.S. 1893, **64**, ii, 563, 566). 16.5° (P. Squire and C. Caines, Pharm. J. 1902, (4), **15**, 413; abst. Chem. Centr. 1902, II, 1434; Jahr. Chem. 1902, 815; J.S.C.I. 1902, **21**, 929). 16.51° (K. Orton, M. Edwards and H. King, J.C.S. 1911, **99**, 1179; abst. C.A. 1911, **5**, 3561; Chem. Zentr. 1911, II, 528; Bull Soc. Chim. 1912, (4), **12**, 23). For viscosity concentration curves for acetic acid and water, see Dunstan and Thole, J.C.S. 1909, **95**, 1559; abst. Chem. Zentr. 1907, I. 1568; Jahr. Chem. 1905-8, 508. For heat of fusion of acetic acid, see R. de Forcrand, C. r. 1903, **136**, 945; abst. J.C.S. 1901, **80**, ii, 372, 594, 641; 1902, **82**, 379; 1903, **84**, ii, 267, 353, 409; Chem. Centr. 1903, I, 1167; Bull. Soc. Chim. 1903, (3), **29**, 907. For heat of liquefaction, see J. Meyer, Festschrift Otto Wallach, 1909, 540; abst. J.C.S. 1910, 98, ii, 182; C.A. 1910, **4**, 1830; J.C.S. 1910, II, 182; Chem. Zentr. 1910, I, 2072; Bull. Soc. Chim. 1911, (4), **10**, 504. For hydrates of acetic acid, see Colles (J.C.S. 1906, **89**, 1252; abst. Chem. Zentr. 1906, II, 1112; Jahr. Chem. 1905-8, 55). For the rate of distillation of acetic acid and formic acids, see H. Richmond (Anal. 1908, **33**, 305; abst. J.S.C.I. 1908, **27**, 897; J.C.S. 1908, **92**, ii, 754; Chem. Zentr. 1908, II, 1087). For binary solution equilibrium between water and acetic acid, see R. Kremann, Bennesch, Flooh and Kerschbaum (Monatsh. 1907, **28**, 893; abst. J.C.S. 1907, **91**, i, 818; Chem. Zentr. 1907, II, 1322; Bull. Soc. Chim. 1908, (4), **4**, 467).

1. L. Lederer, E.P. 26503, 1906; abst. J.S.C.I. 1907, **26**, 1295. F.P. 371358, 1906; abst. J.S.C.I. 1907, **26**, 344; Mon. Sci. 1908, **69**, 150. D.R.P. 191326, 1906. Belg. P. 195837, 1906.

2. E.P. 2511, 1907; abst. J.S.C.I. 1907, **26**, 634; Jour. Soc. Dyers, 1907, **23**, 215. F.P. 376262, 1907; abst. J.S.C.I. 1907, **26**, 988; Mon. Sci. 1908, (4), **68**, 87. D.R.P. 189836, 189837, 1908; abst. Zts. ang. Chem. 1908, **21**, 268; Jahr. Chem. 1905-08, II, 983; J.C.S. 1908,**94**, i, 321; Chem. Ind. 1907, **30**, 617.

3. E.P. 3973, 1911; abst. J.S.C.I. 1911, **30**, 1143, 1156; C.A. 1912, **6**, 2172. F.P. 426436, 1911; abst. J.S.C.I. 1911, **30**, 950. Aust. Appl. A-327, 11, Jan. 12, 1911. Belg. P. 232475, 1911.

4. A. Little, U.S.P 532468, 1895.

5. E. Blumer, D.R.P. 137330, 1901; abst. Chem. Centr. 1903, I, 306; Jahr. Chem. 1903, 1005; Zts. ang. Chem. 1903, **16**, 90. E.P. 10872, 1902; abst. J.S.C.I. 1903, **22**, 642. L. Blumer, F.P. 322206, 1902; abst. J.S.C.I. 1903, **22**, 310. C. Cross and J. Traqualr, U.S.P. 778173, 1904; abst. J.S.C.I. 1905, **24**, 98; E.P. 9868, 1902; abst. J.S.C.I. 1903, **22**, 1008; Mon. Sci. 1904, **60**, 37. W. Wotherspoon, F.P. 334154, 1903; abst. J.S.C.I. 1904, **23**, 29. D.R.P. 182558, 1903; abst. Zts. ang. Chem. 1907, **20**, 178; Mon. Sci. 1909, **70**, 77. Belg. P. 171743, 1903.

hydrocellulose,[1] and of cellulose, best results are obtained when the acetic acid is at least 99% in strength. The uses of acetic acid as inflammable cellulose ester solvent is described in Part Two.

Acetic Anhydride (acetyl oxide, acetic oxide, so-called anhydrous acetic acid) may be prepared by one of the following three modern methods. In the process of T. Goldschmidt,[2] fatty acid anhydrides result by the action of fatty acid salts upon sulfur chloride produced in the reaction by means of dry chlorine upon sulfur, the reaction being carried out either at a low temperature, or up to 40-50°. A mixture of 8 or 9 molecules of sodium acetate with one atomic proportion of sulfur is treated in a closed vessel with 6 atoms of chlorine, the product being then heated to about 80° for 2 hours to convert the acetyl chloride into anhydride.[3] The sulfur may be replaced by ferrous sulfide.[4]

1. M. Althausse, U.S.P. 679204, 1901; abst. Mon. Sci. 1901, **57**, 284. F.P. 304723, 1900; abst. J.S.C.I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1900, **59**, 20. D.R.P. 123121, 1900; abst. J.S.C.I. 1901, **20**, 1133; Zts. ang. Chem. 1901, 14, 905; Chem. Centr. 1901, II, 567; Mon. Sci. 1900, **59**, 9; Jahr. Chem. 1901, 892. E.P. 19039, 1900; abst. J.S.C.I. 1901, **20**, 926.

2. F.P. 25433, 1908; abst. J.S.C.I. 1910, **29**, 112; Chem. Tech. Rep. 1910, **34**, 108. F.P. 407046, 1909; abst. J.S.C.I. 1910, **29**, 112, 517; C.A. 1911, **5**, 1562. Belg. P. 219502, 219909, 1909. D.R.P. 222236, 1908; abst. C.A. 1910, **4**, 2719; Zts. ang. Chem. 1910, **23**, 1390; Chem. Zentr. 1910, I, 1999; Chem. Tech. Rep. 1910, **34**, 275; Chem. Ind. 1910, **33**, 407; Wagn. Jahr. 1910, II, 9. Compare T. Goldschmidt, E.P. 611, 1911. F.P. 407046, 1910; abst. C.A. 1912, **6**, 1849; J.S.C.I. 1911, **30**, 768; 1912, **31**, 152. H. Dreyfus, D.R.Anm. D.-27465. 1912; abst. Kunst. 1913, **3**, 420. D.-27952; abst. Kunst. 1914, **4**, 220. F.P. 448342, 1912, and First Add. Apr. 18, 1913; abst. J.S.C.I. 1913, **32**, 421, 1086.

3. First Add. dated Oct. 16, 1909, to F.P. 407046, 1909; abst. J.S.C.I. 1910, 29, 592. See also F. Bayer & Co., D.R.P. 127350, 1902; abst. Jahr. Chem. 1902, 816; Chem. Centr. 1902, I, 150; Zts. ang. Chem. 1902, **15**, 67; Wagn. Jahr. 1901, II, 8. H. Kessler, F.P. 315938, 1901; abst. J.S.C.I. 1902, **21**, 561; D.R.P. 132605, 1902; abst. Chem. Centr. 1902, II, 167; Zts. ang. Chem. 1902, **15**, 718; Chem. Ind. 1902, **25**, 428; Wagn. Jahr. 1902, 9. Verein f. Chem. Ind. Frankfurt; D.R.P. 161882, 1902; abst.. Zts. ang. Chem. 1905, **18**, 1794; Chem. Zentr. 1905, II, 420; Chem. Ind. 1905, **28**, 482; Wagn. Jahr. 1905, 13. D.R.P. 163103, 1902; Add. to D.R.P. 161882; abst. Chem. Ind. 1905, **28**, 482; Wagn. Jahr. 1905, II, 13.

4. Second Add. dated Dec. 29 1910, to F.P. 407046, 1909; abst. J.S.C.I. 1911, **30**, 768. E.P. 611, 1911; abst. J.S.C.I. 1911, **30**, 152; C.A. 1912, **6**, 1819. D.R.P. 241898, Add. to D.R.P. 222236; abst. C.A. 1912, **6**, 1958, 2291; Zts. ang. Chem. 1912, **25**, 189; Chem.

Or, acetylene, prepared by the action of water on calcium carbide and purified by means of caustic soda and iron salts, is passed into mercuric chloride. The trichloromercuri-acetaldehyde thus formed is converted into aldehyde by boiling with a dilute acid, and the latter into acetyl chloride by treatment with chlorine, this being finally transformed into acetic anhydride by heating with sodium acetate.[1] If the acetaldehyde is treated with chlorous anhydride prepared by the action of chlorine on dry mercuric oxide, acetic anhydride is formed.[2].

In the invention of the Akt. f. Anilin Fabrikation,[3] solutions of sulfuryl chloride in acetic anhydride, obtained by passing sulfur dioxide into chlorine are used to convert anhydrous sodium acetate into acetic anhydride. For example, the solution of sulfuryl chloride obtained by passing 256 parts (by weight) of sulfur dioxide and 284 parts of chlorine into 100 parts of acetic anhydride, is mixed with cooling with 1312 parts dry sodium acetate, the anhydride being distilled off at the completion of the reaction.

Acetic anhydride is a colorless, mobile, highly refractive liquid, having a smell resembling acetic acid but much more irritating. On merely shaking, 12 parts of the anhydride dissolve in 100 parts of cold water,[4] and can be dissolved in

Zentr. 1912, I, 176; Chem. Tech. Rep. 1912, **36**, 107; Wagn. Jahr. 1911, II, 27. See F.P. 315938, 1901.

1. Soc. L'Oyonnithe F.P. 420346, 1910; abst. Mon. Sci. 1913, **78**, 89; J.S.C.I. 1911, 30, 807; C.A. 1912, **6**, 1959; Caout. Gutta-Percha, 1911, **8**, 5236.

2. Soc. L'Oyonnithe, F.P. 442738, 1911; abst. Mon. Sci. 1913, **78**, 141; J.S.C.I. 1912, **31**, 1008; C.A. 1913, **7**, 2835. For purification of acetic anhydride, see G. Ornstein, U.S.P. 1069168, 1913; abst. C.A. 1913, **7**, 3195. For manufacture of acetyl chloride, consult A. Wohl, U.S.P. 710648, 1902; abst. J.S.C.I. 1902, **21**, 1411. E.P. 14032, 1902; abst. J.S.C.I. 1903, **22**, 709.

3. E.P. 23924, 1910; abst. J.S.C.I. 1911, **30**, 48; Chem. Tech. Rep. 1911, **35**, 79. F.P. 421249, 1910; abst. J.S.C.I. 1911, **30**, 423. D.R.P. 244602, 1909; abst. C.A. 1912, **6**, 2294. D.R.P. 273101; abst. Kunst. 1914, **4**, 179; Zts. ang. Chem. 1912, **25**, 751; Chem. Zentr. 1912, I, 1063; Chem. Tech Rep. 1912, **36**, 227; Chem. Ind. 1912, **35**, 223; Wagn. Jahr. 1912, II, 39; J.S.C.I. 1914, **33**, 667. See D.R. Anm. A.-17838; A.-21632; abst. Chem. Ztg. 1912, **34**, 1174. See Naamlooze Vennootschap Fabrik van Chem. Produkten, F.P. 461450, 1913; abst. C.A. 1914, **8**, 2604, for the manufacture of monobasic organic carboxylic acid anhydrides.

4. A. and L. Lumiere and H. Barbier, Bull. Soc. Chim 1906, **35**,

water without completely hydrolyzing.[1] The ability of acetic anhydride to combine with water with the formation of acetic acid, accounts for the development of an acid reaction upon exposure to moist air. When heated with alcohols, the corresponding acetates are formed.

E. Bamberger is of the opinion[2] that in the preparation of acetone from calcium acetate, lime and acetic anhydride are first formed, and the latter then decomposes into acetone and carbon dioxide. In confirmation of this it was found that when acetic anhydride is heated in a sealed tube to about 295° small amounts of acetone, and smaller amounts of acetylacetone are formed. K. Orton and M. Jones[3] have prepared pure acetic anhydride and find the boiling point to be 139.55° at 760 mm., and sp. gr. 1.0876 at 15°/4°, or 1.0820 at 20°/4°. 100 gms. dissolve about 2.7 gms. of water at 15°, the solvent power for water being considerably increased in the presence of small quantities of acetic acid, and diminished by small quantities of sulfuric acid. It does not dissolve cotton, but the latter when soaked in the anhydride at room temperature for 12-24 hours, acetylates much more readily than if not so treated.

According to U. S. Customs Decision, dated June 1, 1905, and June 28, 1905, acetic anhydride, although "not chemically an acid nor scientifically designated as such," is dutiable as

625; abst. J.S.C.I. 1906, **25**, 908; Chem. Centr. 1906, **77**, [(5), **10**], II, 1042; Jahr. Chem. 1905-8, II, 359; J.C.S. 1906, **94**, i, 791. For the hydrolysis of acetic anhydride, and the reaction between acetic anhydride and water in glacial acetic acid, see J. Philip, Proc. Chem. Soc., **28**, 259; abst. C.A. 1913, **7**, 2931.

1. A. and L. Lumiere and H. Barbier, Bull. Soc. Chim. 1905, (3), **33**, 783; abst. Chem. Centr. 1905, II, 465; Jahr. Chem. 1905-8, II, 1664; J.C.S. 1905, **92**, i, 642.

2. Ber. 1910, **43**, 3517; abst. J.C.S. 1911, **100**, i, 103; Chem. Zentr. 1911, I, 295; J.S.C.I. 1911, **30**, 76; Bull. Soc. Chim. 1911, (4), **10**, 1090; C.A. 1911, **5**, 1103. For the rate of hydration of acetic anhydride, see B. Wilsdon and M. Sidgwick, Proc. Chem. Soc. 1913, **29**, 265.

3. J.C.S. 1912, **101**, 1720; abst. J.S.C.I. 1912, **31**, 898; C.A. 1913, **7**, 340; Chem. Zentr. 1912, II, 2055. See S. Young, J.C.S. 1899, **76**, 679; J.S.C.I. 1899, **18**, 859. C. Kahlbaum gives the b. pt. of acetic anhydride at various pressures as follows: 15.02 mm. 44.6 deg.; 25.86 mm., 53.4 deg.; 33.7 mm., 59.0 deg.; 41.24 mm., 62.6 deg.; 53.04 mm., 68.2 deg.; 105.46 mm., 81.2 deg.; 760 mm., 136.4 deg. Faust (Zts. phys. Chem. 1912, **79**, 99), gives the follow-

"acetic acid."[1]

Methods of estimation of acetic acid and acetic anhydride, both alone and together in mixtures, are detailed in Chapter V. For the use of acetic acid and its methyl, ethyl, propyl, butyl and amyl esters as nitrocellulose solvents, consult Part Two. For nitrocellulose-acetic acid lacquers, refer to Part Three.

ing densities, compared with water at 4 deg.; 0°=1.106; 18°=1.0758; 72.5°=1.018.

1. J.S.C.I. 1905, 24, 758, 1044.

CHAPTER II.

MANUFACTURE OF CELLULOSE ESTERS.

Historical. About the year 1860 Paul Schuetzenberger commenced his investigations uopn the acylation of chemical bodies, and published memoirs upon the acetation of cyanogen in 1862 and iodine later in the same year.[1] In 1865 he contributed his research upon the action of acetic acid and acetic anhydride upon various carbohydrates, including normal, or fibrous cellulose.[2] He heated cotton in closed tubes with acetic anhydride to temperatures of 130°-140°, until the former had entirely passed into solution, when the acetated product was precipitated out with water, washed to neutrality, and dried in a partial vacuum over calcium oxide. Thus prepared, the white, amorphous powder was found to be insoluble in water, soluble in alcohol and concentrated acetic acid, readily saponifiable with potash to dextrin and an alkaline acetate, and furnishing nitrogenous products precipable with tannin, upon treatment with ammonia.

Scheutzenberger and L. Naudin[3] four years later, and Scheutzenberger in 1870,[4] materially extended our knowledge of the mechanics of acetation of cellulose, and laid down many of the principles governing the yield and the chemical properties of the acetated cellulose produced. In their preferred method, cellulose (cotton or the filter paper of Berzelius)

1. Comp. rend. 1862, **54**, 154-156, 1026-1029. For biographical sketches of P. Schuetzenberger, see Rev. Gen. Sci. 1897, **8**, 525; Rev. Sci. Paris, 1880, (2), **9**, 629; Rev. Sci. Paris, 1913, **51**, 481.

2. Comp. rend. 1865, **61**, 485-6; abst. Bull. Soc. Chim. 1866, (2), **5**, 291; Zts. Chem. 1866, **9**, 16; Chem. Centr. 1865, **10**, 1036; J. pr. Chem. 1866, **97**, 250; J. Pharm. Chem. 1865, **4**, II, 376; Jahr. Chem. 1865, 594; Ber. 1869, **1**, 163, 556.

3. Comp. rend. 1869, **68**, 814; abst. Chem. Centr. 1869, **11**, 681; Zts. Chem. 1869, **12**, 264; Bull. Soc. Chim. 1868, (2), **10**, 178; 1869, (2), **12**, 107, 204; Jahr. Chem. 1869, 750.

4. Ann. Chim. Phys. 1870, (4), **21**, 235-64; abst. Chem. Centr. 1871, 568; reproduced Ann. Chem. Pharm. 1871, **160**, 74-100; abst. J.C.S. 1872, **25**, 366; Chem. Centr. 1871, 740.

George Wellington Miles

was heated in a closed vessel to 180° with six or eight times its weight of acetic anhydride until a thick syrup results, which, when poured into a large volume of water, precipitates large white flakes of "triacetic cellulose," insoluble in water, alcohol or ether, soluble in concentrated acetic acid, and easily saponified by alkalis with the subsequent regeneration of cellulose.[5] Although it is evident the acetated cellulose obtained by Schuetzenberger was profoundly modified and degraded, yet these experiments aroused the interest, laid the foundation and furnished the generalization upon which subsequent investigations were constructed.

Aime Girard in his investigations upon hydrocellulose in 1875,[1] 1876,[2] 1879,[3] and 1881,[4] laid down many principles of great value in subsequent research and patent litigation, and more specifically referred to under the topic "Hydrocellulose," in Part One.

C. Liebermann and O. Hoermann[5] in their investigations upon the formula of rhamnetin, devised an improvement upon the Schuetzenburger acetation process, in that by heating cellulose with "dephlegmated" (anhydrous) sodium acetate and acetic anhydride under a reflux condenser, a more complete esterification results, no closed tube is required, less

5. Irrespective of the duration of heating or excess of anhydride used, no higher figure by saponification than that corresponding to the tri-acetate was obtained. Using only 2 parts anhydride and heating only to 150°, the cotton inflated without passing into solution, "monacetic and diacetic" esters being formed.

1. Compt. rend. 1875, **81**, 1105; abst. Ber. 1876, **9**, 65; Jahr. Chem. 1875, 786; Chem. Centr. 1876, 83; J.C.S. 1876, **30**, i, 676; Chem. News 1875, **33**, 10.

2. Ann. Chim. Phys. 1876, (5), **9**, 116; abst. Chem. Centr. 1877, 6.

3. Compt. rend. 1879, **89**, 170; abst. Jahr. Chem. 1879, 1116. Compt. rend. 1879, **88**, 1322; abst. Ber. 1879, **12**, 2085, 2158; Jahr. Chem. 1879, 835; Jour de Pharm. 1879, **30**, 348; J.C.S. 1879, **36**, 779. Ann. Chim. Phys. 1881, (5), **24**, 337; abst. Ber. 1881, **14**, 2834; Jahr. Chem. 1881, II, 985; J.C.S. 1882, **42**, 378.

4. For "Conversion of Hydrocellulose into Pyroxylin," see Girard, Compt. rend. 1879, **89**, 170; abst. J.C.S. 1879, **36**, 911. Same as Bull. Soc. d'Encour., (3), **8**, No. 91; abst. Chem. News 1881, **44**, 216.

For life of A. Girard see M. L. Lindet, Bull. Soc. Chim. 1898, (3), **20**, I-XXVI, with bibliography.

5. Ber. 1878, **11**, 1618; abst. J.C.S. 1879, **36**, 271; Bull. Soc. Chim. 1879, **32**, 338; Jahr. Chem. 1878, 92; Chem. Centr. 1878, 710.

bye-products are obtained, acetylation can be conducted at lower temperatures with a considerably higher quantitative yield of acetylated compound.

A. Franchimont, in 1879, in repeating the work of Liebermann, was unable to obtain a reaction between sodium acetate, acetic anhydride and cellulose (Swedish filter paper), at least the cellulose did not dissolve.[6] He regarded sodium acetate as of value as a probable dehydrating agent only, and from this reasoned that a more energetic dehydrating body, such as sulfuric acid, would be correspondingly more efficient. It was found that when a little sulfuric acid is added to a mixture of one part of cellulose and four parts of acetic anhydride, brisk action immediately commences, even without the application of external heat, and the cellulose goes into solution, forming a viscous and colored liquid, from which the acetylated cellulose may be recovered by pouring into water and washing free from uncombined acid. The product after purification from hot ethyl alcohol gave upon elementary analysis figures corresponding to an eleven times acetylated triglucose. When fused zinc chloride was substituted the reaction was less energetic, the final solution being colorless, from which a white amorphous powder was precipitated which gave analytical figures corresponding to triacetylcellulose. With sulfuric acid as the condensing agent, Franchimont was able to obtain at least two dissimilar bodies, as indicated by their solubility in oht and cold ethyl alcohol, whereas when the sulfuric acid was substituted by zinc chloride, only the derivative soluble in hot alcohol was formed, while the colorless acetylating solution showed that the cellulose decomposition had been less far-reaching.[7]

C. Guignet, in his investigations of artificial parchment and

6. Rec. Trav. Chim. 1899, (2), **18**, 465, 472; abst. J.C.S. 1900, **78**, i, 141; Jahr. Chem. 1899, 1289. Rec. Trav. Chim. 1883, **2**, 241; abst. Jahr. Chem. 1883, 1366; Chem. Centr. 1884, 60.

7. Compt. rend. 1881, **92**, 1053; abst. Chem. Centr. 1881, 424; Jahr. Chem. 1881, 985; J.C.S. 1881, **40**, 709; Ber. 1881, **14**, 1290. Compt. rend. 1881, **92**, 1054; abst. Chem. Centr. 1881, 422; Jahr. Chem. 1881, 859; J.C.S. 1881, **39**, 716; Ber. 1881, **14**, 1284. Compt. rend. 1879, **89**, 711; abst. J.C.S. 1880, **38**, 159; Chem. Centr. 1879, 771. Reproduced Ber. 1879, **12**, 1938.

the action of sulfuric acid upon cellulose[1] by impregnation, accumulated considerable data, which was extended by subsequent workers.

E. Erwigs and W. Koenigs in their investigations of the acetyl derivatives of quinic acid,[2] and pentacetyl dextrose,[3] galactose[4] and levulose,[5] studied the acetylation method proposed by Franchimont in 1879, in which zinc chloride was added to the acetic anhydride in place of sulfuric acid or sodium acetate. The subject was next advanced by C. Cross and E. Bevan,[6] who, following the method of Franchimont, heated acetic anhydride to the boiling point, dropped in a fragment of zinc chloride, after which the specially purified fibrous cotton was added in successive small portions, the digestion being continued from two to three days. Preliminary observations on the crude ester of the reaction, separated by treatment of the filtered solution with water, showed them that the acid found by saponification was considerably in excess of the quantity theoretically obtainable from triacetylcellulose.

1. Compt. rend. 1889, **108**, 1258; abst. Jahr. Chem. 1889, 2839; Ber. 1889, **22**, 574; Chem. Centr. 1889, II, 124; J.C.S. 1889, **51**, 847; Chem. News 1889, **60**, 24.

2. Ber. 1889, **22**, 1457; abst. J.S.C.I. 1889, **8**, 723; Jahr. Chem. 1889, 1692; J.C.S. 1889, **56**, 991; Chem. Centr. 1889, **60**, 251.

3. Ber. 1889, **22**, 1464; abst. J.S.C.I. 1889, **8**, 718; Jahr. Chem. 1889, 2041; J.C.S. 1889, **56**, 952; Chem. Centr. 1889, **60**, 250.

4. Ber. 1889, **22**, 2207; abst. J.S.C.I. 1889, **8**, 994; Jahr. Chem. 1889, 2041; J.C.S. 1889, **56**, 1131; Chem. Centr. 1889, **60**, 748.

5. Ber. 1890, **23**, 672; abst. J.S.C.I. 1890, **9**, 637; Jahr. Chem. 1890, 2132; J.C.S. 1890, **58**, 732; Chem. Centr. 1890, **61**, 757.

6. Chem. News, 1889, **60**, 163, 254; abst. Chem. Centr. 1889, **60**, II, 790; 1890, **61**, 21; Jahr. Chem. 1889, 2066; 1890, 2152. See also Cross and Bevan, J.C.S. 1890, **57**, 2; abst. Chem. Centr. 1890, **61**, I, 390; Amateur Photog. 1899, **30**, 146; Tech. Repert. 1889, 45. For zinc chloride solvent of cellulose, see their Chem. News, 1891, **63**, 66; abst. Chem. Centr. 1891, **62**, I, 534; Jahr. Chem. 1891, 890; Ber. 1891, **24**, 401. J.C.S. 1904, **85**, 691; abst. Bull. Soc. Chem. 1904, (3), **32**, 1801. In J.C.S., 1890, **57**, 1, in the course of investigations on the constitution of the lignocelluloses (J.C.S., 1889, **55**, 199) action of acetic anhydride on jute was studied, and on boiling purified cotton for sixteen hours with acetic anhydride containing a trace of zinc chloride in solution, the whole of the fiber had disappeared, and on pouring the solution into water a copious precip'tate was obtained, which, after washing and drying, gave on hydrolysis a quantity of acetic acid equivalent to 80% of the substance.

The product obtained was purified by solution in glacial acetic acid, the solution being limpid and not gelatinous as stated by Franchimont in the case of the triacetylcellulose which he was able to prepare. Upon filtering the solution, washing the flocculent precipitate thereby obtained with sulfurous acid, combustions gave 51.6% and 52.3% respectively of carbon and 5.8% and 5.6% of hydrogen, whereas the carbon percentage calculated for the triacetylcellulose is 50.0%, and for the pentacetylcellulose 51.6%. Determination of acetic acid by saponification gave from 79%-82%, the percentages calculated for tri-, tetra-, and pentacetylcellulose being 62, 73 and 81 respectively. They embodied the results of their experiments in a patent in 1894,[1] in which cellulose hydrate prepared from precipitation of solutions of cellulose in zinc chloride, or cuproammonium or from viscose, was heated with crystallized zinc acetate and acetyl chloride, the product being soluble in chloroform, from which transparent coherent pellicles were obtained from evaporation, and which suggested to the inventors the use of acetated cellulose for the replacement of collodion in pharmacy and surgery. C. Weber,[2] working along similar lines to Cross and Bevan, produced an acetylated cellulose by means of magnesium acetate and acetyl chloride which was described as insoluble in methyl or ethyl alcohols, ethyl acetate, amyl acetate, acetone and ether, but soluble in ethyl benzoate, chloroform, acetic anhydride and acetic acid, and in ethyl benzoate, nitrobenzene and epichlorhydrin. On account of the non-inflammability, resistance to moisture and high temperature and their high insulating capacity, Weber predicted the acetylcelluloses would soon become powerful rivals of celluloid, a prediction that at the present time appears to be far from general realization.

J. Thiele in investigating the action of acetic anhydride upon quinone and dibenzoylstyrene[3] employed one part of

1. E.P. 9676, 1894; abst. J.S.C.I. 1895, **14**, 987; Chem. Centr. 1896, I, 465.

2. Zts. ang. Chem. 1899, **12**, 5; abst. Proc. Amer. Pharm. Assoc. **48**, 786; Chem. News, 1899, **80**, 247; Jahr. Chem, 1899, 1289; Wagn. Chem. 1899, **45**, 1065; Chem. Centr. 1899, **70**, 337.

3. Ber. 1898, **31**, 1247; abst. J.C.S. 1899, **74**, 1, 469; Chem.

sulfuric acid to 40-45 parts of acetic anhydride. Z. Skraup studied the action of sulfuric acid as an aid in acetylation, and found by successive experiments that he was able to attenuate the amount of sulfuric acid to cellulose to 0.01% of the weight of acetic anhydride in the case of mucic acid, and still produce tetraacetylmucic acid equivalent to 79% of the amount theoretically possible. Only amorphous products were obtained when acetic anhydride and anhydrous sodium acetate was employed. When traces of sulfuric acid only were used (0.0001%) the reaction goes on but is probably incomplete.[1] It was Skraup who first made clear that where relatively smaller amounts of sulfuric acid is employed, and the acetylation carried on at lower temperatures, compounds of a more complicated nature are more often obtained than when the quantity of sulfuric acid is increased and the temperature raised.

L. Vignon and E. Guerin in their researches upon the acetyl compounds of cellulose and acetylcellulose,[2] undertaken primarily to determine the alcoholic character of cellulose, acetic anhydride 100 gms., and zinc chloride, 2 gms., were previously mixed and heated to boiling on a paraffin bath, and cotton previously dried at 100°, added by degrees in successive tufts, the mixture being maintained at the boiling temperature for a period of 16 hours. The solution became

Centr. 1898, **69**, 11, 31; Jahr. Chem. 1898, 2010; Bull. Soc. Chim. 1898, (3), **20**, 596. See also Saruw, Ann. 1881, **209**, 129. Buchk, Ber. 1881, **14**, 1327. H. Schultz, Ber. 1882, **15**, 652. Hinsberg, Ber. 1894, **27**, 3259.

1. Monats. 1898, **19**, 458; abst. J.C.S. 1899, **76**, i, 112; Bull. Soc. Chim. 1898, (3), **20**, 898; Jahr. Chem. 1898, 1123; J.S.C.I. 1898, **17**, 895. Ber. 1899, **32**, 2413; abst. J.C.S. 1899, **76**, i, 852; J.S.C.I. 1899, **18**, 941; Chem. Centr. 1899, II, 2140; Jahr. Chem. 1899, 1288; Bull. Soc. Chim. 1900, (3), **24**, 619. Annuario Soc. chim. 1899, 27. Ber. 1901, **34**, 1115; abst. Bull. Soc. Chim. 1902, (3), **28**, 317; Jahr. Chem. 1901, 878; Chem. Centr. 1901, **72**, I, 1197, J.C.S. 1901, **80**, i, 370. Skraup and J. Koenig, saponified the crystalline acetate obtained by the method of Franchimont by the action of acetic anhydride on cellulose in the presence of sulfuric acid, the acetate being saponified by alcoholic potash, and yielding ordinary glucose upon inversion.

2. Compt. rend. 1900, **131**, 588; abst. J.S.C.I. 1900, **19**, 1103; J.C.S. 1900, **78**, i, 629; Jahr. Chem. 1900, 843; Chem. Centr. 1900, **71**, 1069; Bull. Soc. Chim. 1901, (3), **25**, 189; abst. Jahr. Chem. 1901, 891; Chem. Centr. 1902, **71**, 440; Fahrerber. Chem. 1901, **2**, 891.

brown and finally blackened, the cotton passing into solution after 25 minutes. This is evidence of profound decomposition of the cellulose. The acetylation of oxycellulose gave a yield of 40% of a dark, readily reducible product, insoluble in water, alcohol or ether, but readily passing into solution in acetic acid. Combustion determinations gave figures indicating the product obtained to be probably a triacetyl derivative.

In a communication made in the name of the Committee of the Economic Arts of France on viscose and viscoid and presented by C. Bardy [1] in 1900, is reviewed the various steps taken in the development of the field of acetylcellulose to that time, and especially the products developed by Cross, Bevan and Weber.

H. Ost has made careful and exhaustive studies of the mechanics of cellulose esterification [2] and especially the three following processes of cellulose acetylation, viz.:

Cross and Bevan's process by the action of zinc acetate and acetyl chloride, Lederer's process by the action of acetic anhydride and sulfuric acid on hydrocellulose, and Bayer's process by the action of the same reagents on normal cellulose, all yield the same product, triacetylcellulose $C_6H_7O_5(C_2H_3O)_3$. At the same time, the author is inclined to doubt whether a triacetate of normal cellulose really exists, and to regard these products as the triacetates of a series of hydrocelluloses of varying degrees of degradation, the position of any member in the series being determined by the relative viscosity of its solution, and the elasticity of its films. The author estimates that the relation of such a hydrocellulose to the normal cellulose may be expressed by the fixation of hydrolysis of 1 mol. of water on to 6 mols. of cellulose. The incipient hydrolysis of the cellulose which appears to be a condition necessary for the esterification, may be effected either simultaneously, as in Bayer's process, or in a separate preliminary operation, as

1. Bull. Soc. d'Encourag. 1900, (5), **5**, 321.

2. Zts. ang. Chem. 1906, **19**, 993; abst. J.S.C.I. 1906, **25**, 606; Jahr. Chem. 1905-8, 983; Chem. Centr. 1906, II, 672. Zts. ang. Chem, 1911, **24**, 1304; abst. Chem. Zentr. 1911, II, 750; J.S.C.I. 1911, **30**, 1247; J.C.S. 1911, **99**, i, 712; C.A. 1912, **6**, 1671. For polemical by Eichengruen, see Zts. ang. 1911, **24**, 13, 6; abst. Chem. Zentr. 1911, II, 750.

in Lederer's process. The author contends that the cellulose acetate obtained by Cross and Bevan's process is not a tetracetate as asserted by the discoverers, but a triacetate identical with the other products. The error which is thus stated to exist in the latter author's work is attributed to the fact that the saponification of these esters by boiling aqueous-alcoholic potash is accompanied by the production of acids at the expense of the cellulose residue, and that the results of saponification are too high. The author prefers to effect the hydrolysis by means of equal volumes of sulfuric acid and water, acting in the cold for about 48 hours, and to distil off the acetic acid in a current of steam for 4-5 hours. The production of all these triacetates is preceded by the production of diacetates, which can be isolated by stopping the reaction whilst still incomplete. The analogy between the acetates and nitrates of cellulose is complete; in both cases the highest limit of esterification corresponds with the substitution of three hydroxyl groups in each C_6 unit, the products not being esters of normal cellulose but of modified, hydrolysed, or oxidised derivatives of cellulose.

In 1905 appeared an article by F. Marsden [1] upon acetylcellulose which with the 26 bibliographical citations and the appended discussions presents a summary of the subject to that date. C. Haeussermann [2] nitrated acetylcellulose in the formation of mixed esters, and was able to obtain after 14 days action of nitric acid of sp. gr. 1.52, a white powder containing 11.5% of nitrogen.

In the acetylation of various oxycelluloses as carried out by E. v. Hardt-Stremayr,[3] and obtained by the oxidation of wood, cotton and paper, all gave the same cellobiose octacetate (m. pt. 228°) as is obtained from cellulose itself. Calculated on the percentage of the original material, the yields were: From pure cellulose, 25%; from hydralcellulose prepared with

1. Jour. Soc. Dyers and Col. 1905, **21**, 100.

2. Chem. Ztg, 1905, **29**, 667; abst. Zts. ang. Chem. 1905, **18**, 1989; Chem. Centr. 1905, II, 760; Wagn. Jahr. 1905, II, 192.

3. Monats. Chem. 1907, **28**, 73; abst. Bull. Soc. Chim. 1908, (4), **4**, 5; J.C.S. 1907, **92**, i, 389; Zts. ang. Chem. 1908, **21**, 1186; Chem. Centr. 1907, I, 1571; C.A. 1907, **1**, 2180. Wien. Akad. Ber. **116**, 2-b, 13; Jahr. Chem. 1905-8, II, 923.

hydrogen dioxide, 25%; from oxycellulose prepared from nitric acid, 16%; from oxycellulose prepared from potassium chlorate and hydrochloric acid, 10%, and from acid-cellulose prepared from acidified Schweitzer's solution, 7%.

In the field of purely theoretical chemistry, E. Knoevenagel has sought to clear up some phases of acetylation by an investigation of the colloidal nature of acetylcellulose,[1] and a determination of the influence of the following series of catalyzers upon the acetylation of the C:O group by acetic anhydride; ferric, zinc and stannous chlorides and phosphorus trichloride; ferrous, cupric, zinc, ammonium and dimethylamine sulfates; and sulfuric and sulfonic acids.[2]

A. Smith and K. Orton in investigating the role of acids as accelerators in acetylation, have measured the speed of acetylation of *s*-tribromphenol in the presence of sulfuric, phosphoric and perchloric acids, and have found that whereas in acetic acid and chloroform solution, acetic anhydride has no

1. Chem. Ztg. 1911, **36**, 248; abst. C.A. 1912, **6**, 1671; Kunst. 1914, **4**, 232.

2. Ann. 1914, **402**, 111; abst. J.S.C.I. 1914, **33**, 102; C.A. 1914, **8**, 913. He found that the acetylation of hydroxyl groups with acetic anhydride can be accelerated and often carried out almost quantitatively at ordinary temperatures by the addition of 1 to 5 per cent. of certain substances (ferric, zinc and stannous chlorides, phosphorus trichloride, sulfuric acid, copper sulfate, ammonium sulfate, etc.) which behave, not as dehydrating agents, but in some unexplained way as catalysts. Substances containing carbonyl oxygen, and ethereal or anhydride-like bodies such as ethers, polysaccharides, celluloses and starches, and oxygen ring compounds as epichlorhydrin, cineol ,etc., can also by the breaking of an oxygen linkage be similarly converted into diacetates (called "acetolysis" in contradistinction to hydrolysis). The catalysts appear to be specific in their action, so that by using a suitably selected catalyst with, for example, cellulose, it may be possible either to acetylate hydroxyl groups, or split the molecule by acetolysis at specific positions favourable for attack by the catalyst employed. The acetylation of a number of different types of substances has been studied in detail, using the catalysts mentioned above. All except ammonium sulfate convert aldehydes into diacetates. Quinone and unsaturated ketones react best in presence of ferric chloride. Diethyl ether and three-membered oxygen carbon rings react only with ferric chloride, the former at 100°, the latter at the ordinary temperature. In contrast to this, six-membered rings, such as cineol, readily yield acetates, in presence of nearly all the catalysts, by the splitting of the ring at the oxygen atom. Salicylic aldehyde with acetic anhydride and phosphorus trichloride, copper sulfate or zinc sulfate, was converted into disalicylic aldehyde, whilst the other catalysts yielded mainly the triacetate.

perceptible action on *s*-tribromphenol at the ordinary temperature, even after keeping for several weeks, in the presence of perchloric and sulfuric acids, acetylation takes place very rapidly. Orthophosphoric acid (or phosphoric oxide) comes far behind as an accelerator. When the quantity of acid is small, the rate of the reaction is approximately proportional to its concentration. Comparing gram-molecular proportions, perchloric acid is about 2-5 times as effective as sulfuric acid. Chloroform is the medium in which acetylation is the most rapid, but acetic acid is only slightly inferior. Benzene and acetone are unfavorable to acetylation. A comparison of pyridine, acids, and sodium acetate as accelerators of acetylation by acetic anhydride, shows that both the two former are far superior. Pyridine is approximately as effective as perchloric acid and therefore superior to sulfuric acid.[1]

A. Green and A. Perkin[2] and A. Green[3] have investigated the products of cellulose acetylation in order to throw light on the composition and constitution of the ester of maximum acetation. Various acetylated celluloses are determined for their acetic acid content by methods of both acid and alkaline saponification, the results all clearly pointing to the triacetate as the highest acetylated cellulose ester.

The work of A. Eichengruen,[4] G. Miles,[5] and other inventors and patentees are reviewed in detail elsewhere. C. Schwabe,[6] W. Main,[7] E. Fischer,[8] J. Beltzer,[9] M. Mat-

1. Proc. C.S. 1909, **25**, 166. J.C.S. 1909, **95**, 1060; abst. J.S.C.I. 1909, **28**, 678; Jahr. Chem. 1909, 607; Bull. Soc. Chim. 1909, (4), **6**, 893; Chem. Zentr. 1909, II, 515.

2. J.C.S. 1906, **89**, 811; abst. Bull. Soc. Chim. 1910, (4), **2**, 37; Jahr. Chem. 1905-8, II, 985; Zts. ang. Chem. 1907, **20**, 459; Chem. Centr. 1906, II, 821.

3. Zts. Farb. Text. Ind. 1904, **3**, 97; abst. Chem. Centr. 1904, I, 1069; Jahr. Chem. 1904, 1160, 1161.

4. Zts. ang. Chem. 1911, **24**, 1306; abst. Chem. Zentr. 1911, **82**, II, 750. For "Acetylization with sulfuric acid and acetic anhydride," see J. Blanksma, Chem. Weekblad. **6**, 717; abst. C.A. 1910, **4**, 752; Jahr. Chem. 1909, 494; Chem. Zentr. 1909, **80**, 1210, J.C.S. 1909, **96**, i, 779.

5. U.S.P. 838350, 1906; Reissue 12637, 1907.

6. Jour. Soc. Dyers and Col. 1914, **30**, 13; abst. J.S.C.I. 1914. **33**, 131.

7. Rev. Scien. 1912, **50**, 783. Chimiste, 1912, **3**, 41, 43; abst C.A. 1912, **6**, 1849. Compilation. See Marsden, Farb. Ztg., 1906, **42**, 172.

thews,[1] F. Bowman,[2] H. Mork,[3] W. Walker,[4] G. Noyer,[5] and L. Clement and C. Riviere[6] have published summaries of the state of the art, comprising mostly compilations. The various methods of manufacture which have been proposed from time to time, the solvents and thermoplastic-inducing bodies advocated and the technical applications of the cellulose esters are detailed in separate sections.

C. Schwalbe[7] has shown that the production of soluble acetyl derivatives of cellulose by the action of acetic anhydride and glacial acetic acid on cellulose, always requires the presence of a so-called catalytic agent. The catalytic agents specified in a very large number of patents may be classed under three heads, viz.: Free mineral acids, weaker acids and acid salts, and neutral salts which are readily dissociated. The author discusses the mechanism of these reactions and points out that the production of the cellulose acetate is invariably accompanied by a more or less profound modification of the cellulose, with the production of hydrocellulose, as evidenced

8. Kunst. 1912, **2**, 21, 48, 64; 1914, **4**, 102, 123; abst. C. A. 1912, **6**, 2314; 1914, **8**, 1871; Wagn. Jahr. 1912, II, 445; Zts. ang. Chem. 1912, **25**, 507, 1549; Chem. Tech. Rep. 1912, **86**, 307. Compilation of 236 cellulose ester patents chronologically arranged.

9. Rev. gen. Chim. pure et appl. **9**, 421; abst. Chem. Zentr. 1907, **78**, I, 853; Jahr. Chem. 1905-8, II, 983; Zts. ang. Chem. 1907, **20**, 1537. Mon. Sci. 1908, (4), **22**, 529, 648; 1910, (4), **24**, 145; abst. Jahr. Chem. 1905-8, 990; J.S.C.I. 1908, **27**, 1037; Chem. Zentr. 1910, II, 509; C.A. 1910, **4**, 1238; Zts. ang. Chem. 1908, **21**, 741. See also R. Bernard, Mon. Sci. May 1905, page 22.

1. "The Textile Fibers," 1913, 221.

2. "Structure of the Cotton Fibre," 1908, 197.

3. Original Communication, 8th Inter. Cong. Appl. Chem. **18**, 195; abst. C.A. 1912, **6**, 3013; Kunst. 1913, **3**, 273.

4. Jour. Frankl. Inst. 1907, **144**, 131; abst. Mon. Sci. 1908, **68**, 461.

5. Caout. et Guttap, 1913, **10**, 6875; abst. Kunst. 1913, **3**, 352.

6. Original Communication, 8th Inter. Cong. Appl. Chem. **9**, 59; abst. J.S.C.I. 1912, **31**, 869; C.A. 1912. **6**, 3182; Kunst. **2**, 436.

7. Zts. ang. Chem. 1908, **21**, 2401; abst. Bull. Soc. Chim. 1909, (4), **6**, 231. Zts. ang. Chem. 1910, **23**, 433; abst. J.C.S. 1910, **88**, i, 224; Bull. Soc. Chim. 1910, (4), **8**, 694. Reproduced, E. Worden, "Nitrocellulose Industry," 1911, **2**, 1037. Zts. ang. Chem. 1911, **24**, 1256; abst. Wagn. Jahr. 1911, II, 504; J.S.C.I. 1910, **29**, 415; 1911, **30**, 948; C.A. 1912, **6**, 42; J.C.S. 1911, **99**, i, 712. In Chem. Ztg. 1910, **34**, 1351, K. Schwalbe recommends hydrolyzed cellulose acetate in solution as a protection of drying cylinders from rust and erosion.

by the cupric-reducing properties of the cellulose residue after saponification of the ester. Of the mineral acid group of catalytic agents, sulfuric acid is by far the most important, and its application is sufficiently illustrated by the patents of Lederer and of Bayer and Co. The principal representatives of the second group are the phenolsulphonic acid of Mork's patent and the halogenated fatty acids of Knoll & Co. The author attributes the catalytic effect of these bodies to the presence of limited quantites of free mineral acid either as an impurity in the original substance or as the product of its dissociation in the presence of cellulose at the temperature of the reaction. Representatives of the third group are found chiefly in Knoll and Co.'s patents and include such bodies as ferrous sulfate, ferric chloride, diethylamine sulfate, ammonium sulfate, etc. Here again it is pointed out that these so-called neutral salts contain weak bases and that free mineral acids are produced from them by dissociation, which is peculiarly favoured by the presence of the cellulose and the high temperature necessary for the reaction.

Investigations of Stein. A. Stein[1] in a dissertation upon the fatty acid esters of hydrocellulose and their saponification, published Dresden in 1911, and reproduced in Zts. ang. Chem. 1913, **26**, 673 et seq, has made most extensive and apparently accurate determinations of the mechanics of fatty acid esterification as applied to cellulose, but especially hydrocellulose, the conclusions of which are indicated herewith somewhat in *extenso*.

Hydrocellulose as obtained by the action of mineral acids upon cellulose has been the subject of many investigations, Girard,[2] Ost,[3] Koerner,[4] and Buettner and Neumann[5] following the original method of Girard—saturating fibrous cellulose with sulfuric acid of 3%-4%, pressing, drying and heating in a closed vessel to 70°. They found upon ultimate analysis that hydrocellulose contains more water than normal

1. Zts. ang. Chem. 1913, **26**, 673; abst. Kunst. 1914, **4**, 94.
2. Ann. Chim. Phys. 1881, (5), **24**, 360.
3. Zts. ang. Chem. 1906, **19**, 994.
4. Dissertation, Dresden, 1907, p. 24.
5. Zts. ang. Chem. 1908, **21**, 2609.

or fibrous cellulose, and that therefore the latter has undergone hydrolytic decomposition in passing into hydrocellulose. Stein obtained 44.9-44.65 as the percentage of carbon obtained from the hydrocellulose prepared by himself, the cotton used being previously dried at 120°.

In the following table is given the percentages of carbon and hydrogen in various theoretically possible hydrocelluloses, together with the actual percentages found by the investigators named.

TABLE I.

HYDROCELLULOSE.	THEORY.		FOUND.		MATERIAL.	OBSERVER.
	%C.	%H.	%C.	%H.		
$(C_6H_{10}O_5).2H_2O$	36.34;	7.12	38.59;	6.50;	Cotton;	Koerner.
$(C_6H_{10}O_5).H_2O$	39.98;	6.72	41.8 ;	6.7 ;		Girard.
$(C_6H_{10}O_5)_2.H_2O$	42.08;	6.48				
$(C_6H_{10}O_5)_3.H_2O$	42.84;	6.40	42.83;	6.41;	Cotton;	Buettner and [Neumann.
$(C_6H_{10}O_5)_4.H_2O$	43.22;	6.35				
$(C_6H_{10}O_5)_5.H_2O$	43.46;	6.33	43.48;	6.24;	Paper;	Buettner, Ost.
			43.54;	6.39;	Paper;	Ost.
$(C_6H_{10}O_5)_6.H_2O$	43.61;	6.31				
$(C_6H_{10}O_5)_7.H_2O$	43.73;	6.30				
$(C_6H_{10}O_5)_8.H_2O$	43.81;	6.29				
$(C_6H_{10}O_5)_9.H_2O$	43.88;	6.28	43.86;	6.41;	Cotton;	Buettner, Neu- [mann.
$(C_6H_{10}O_5)_{10}.H_2O$	43.93;	6.27				
$(C_6H_{10}O_5)_{11}.H_2O$	43.98;	6.27				
$(C_6H_{10}O_5)_{12}.H_2O$	44.015;	6.265				
$(C_6H_{10}O_5)_{12}.H_2O$	44.42;	6.22	44.32;		Cotton;	Stein.

The above analytical data indicates that hydrolysis cannot be proven in the hydrocellulose prepared according to Girard by ultimate analysis alone, but does not preclude that hydrolysis has occurred. Recent publications[1] support the latter view.

For the formation of the hydrocellulose esters of the homologues of acetic acid, the introduction of hydrocellulose into a mixture of acid anhydride and concentrated sulfuric acid is recommended,[2] the temperature being reduced to that of the room, and left with occasional shaking for 24 hours, precipitated with dilute alcohol or water, purified by extraction with chloroform, and the filtrate evaporated to dryness.

1. Ost, Zts. ang. Chem. 1912, **25**, 1996. Ann. 1913, **398**, 313. Klein, Dissertation, Hannover, 1913, p. 79.
2. Lederer, D.R.P. 118538. F. Bayer & Co., D.R.P. 159524.

The analytical data of the hydrocellulose propionate, butyrate and *iso*-valerate thus prepared, all pointed to hydrolytic decomposition, increasing with the concentration of the sulfuric acid. The decomposition may only be apparent, as Ost [1] and Eichengruen [2] have shown that high molecular cellulose esters part with their moisture only with difficulty.

In order to determine to what extent other catalytic substances other than sulfuric acid participate in the reaction or even enter into permanent combination, mono- and trichloracetic acids were used.[3] The hydrocellulose acetates and butyrates thus obtained when submitted to analysis showed that the hydrocellulose esters prepared with the chloracetic acids contain variable small amounts of chlorine in chemical union. Combustions gave results in general lower than the theory as indicated in Table II.

TABLE II.

	THEORY.		
Acetylhydrocellulose:	%C.	%H.	% ACm.
$(C_6H_9O_4(CO_2CH)_3)_n.H_2O$	47.04	5.93	29.4
$(C_6H_9O_4(CO_2CH)_3)_6.H_2O$	46.35	6.00	29.0
$(C_6H_8O_3(CO_2CH_3)_2)_n.H_2O$	48.76	5.73	48.8
$(C_6H_8O_3(CO_2CH_3)_2)_6.H_2O$	48.17	5.80	48.2
$(C_6H_7O_2(CO_2CH_3)_3)_n.H_2O$	49.98	5.60	62.5
$(C_6H_7O_2(CO_2CH_3)_3)_6.H_2O$	49.46	5.66	61.8
Butyrylhydrocellulose:			
$(C_6H_9O_4(CO_2C_3H_7)\ )_6.H_2O$	....	....	37.5
$(C_6H_8O_3(CO_2C_3H_7)_2)_6.H_2O$	....	....	57.7
$(C_6H_7O_2(CO_2C_3H_7)_3)_6.H_2O$	....	....	70.4

Klein [4] has claimed on the ground of his exhaustive investigations that the values of 65.5% and 66.0% are too high, because cellulose acetates with more than 62.55% acetic acid must dissolve in alcohol. On the other hand, Ost and Katayama [5] describe an acetylated cellulose with 64.5% acetic acid which dissolves completely in acetone.

H. Muschner [6] has reviewed the general subject of cellulose esters of organic and inorganic acid radicals, and

1. Ann. 1913, **398**, 323
2. Zts. ang. Chem. 1911, **24**, 366.
3. D.R.P. 198482, 203642.
4. Zts. ang. Chem. 1912, **25**, 1409.
5. Zts. ang. Chem. 1912, **25**, 1467.
6. Dissertation, Berlin, 1913, 54 pages.

comprising the cellulose formates, benzoates, and the combinations of hydrocellulose with *m*-nitrobenzoyl chloride, *p*-chlorbenzoyl chloride, *p*-brombenzoyl chloride, *p*-toluyl chloride, and the cellulose chlorbenzoates.

Chemistry. The chemistry of the acetic esters of cellulose has not been as exhaustively investigated as the corresponding nitric esters. Accepting the formula of cellulose in its simplest terms ($C_6H_{10}O_5$) the acetylated derivatives of cellulose would possess the following formulas:

Cellulose mono-acetate, $C_6H_9O_4$ $(O.CO.CH_3)$.

Cellulose di-acetate, $C_6H_8O_3$ $(O.CO.CH_3)_2$

Cellulose tri-acetate, $C_6H_7O_2$ $(O.CO.CH_3)_3$

In the acetation of cotton, however, as with the formation of the corresponding nitrates, the esterification is not a simple process of substitution of acid radical for cellulose hydroxyl, as appears from the above formulas. Cellulose compounds in general exhibit so many solubility peculiarities and other variations that it is not surprising that the acetic esters, under different temperature conditions and esterizing compositions, should yield products of varying physical deportment. It appears that the researches of Eder,[1] Vieille,[2] Mendeleeff,[3] Bruehl, Lunge[4] and others, have demonstrated for the corresponding nitric esters that at least twelve acid radicals may be introduced into the cellulose aggregate. Acetylcellulose has an added complexity as compared with nitrocellulose, in the process of partial hydration, preceding, coincident with, or succeeding the normal acetation process, whereby an indeterminate number of other products result, as judged by solubility and saponification determinations.

1. Ber. 1880, **13**, 169; abst. Jahr. Chem. 1880, 1005; Chem. Centr. 1880, 170; Bull. Soc. Chim. 1881, 179; J.C.S. 1880, **38**, 372. See W. Walker, Jour. Frankl. Inst. 1907, **144**, 131.

2. Compt. rend. 1883, **95**, 132; abst. Bull. Soc. Chim. 1883, **1**, 527. See also L. Vignon, Compt. rend. 1903, **136**, 818.

3. Mon. Sci. 1897, **49**, 510; abst. Engineering, Feb. 5, 12, 19, 1897.

4. G. Lunge and Bebie, J.A.C.S. 1901, **23**, 528; abst. Zts. ang. Chem. 1901, **14**, 483, 507, 537; Chem. News 1901, **84**, 301; Wagn. Jahr. 1901, I, 495; Chem. Centr. 1901, II, 764; 1899, I, 1272; 1901, II, 34, 92; Jahr. Chem. 1901, 893. Lunge and Weintraub, Zts. ang. Chem. 1899, **12**, 393, 441, 467; Chem. Centr. 1899, I, 1272; Jahr. Chem. 1899, 1302; J.C.S. 1899, **76**, i, 559; Wagn. Jahr. 1899, 425.

There are also cellulose acetates analytically indistinguishable, separable by physical means.

The following esters have been more or less thoroughly investigated:

Cellulose Mono-acetate is formed by the superficial or incomplete acetylization of cellulose, as by boiling cotton with acetic anhydride in the presence of sodium acetate and without the presence of a mineral condensing agent, the structure of the cellulose remaining unchanged. The mono-acetate is said to be insoluble in all solvents of the higher acetates and in those of cellulose. It is entirely insoluble in all the solvents of the higher acetates, resists the action of such special solvents of cellulose as zinc chloride and cupro-ammonium, and in other respects is equally stable and inert. The hygroscopic moisture under ordinary atmospheric conditions is 3.2%.

Cellulose Diacetates have been described as obtainable from the action of acetic anhydride on cotton in the presence of small amounts of such hydrolyzing agents as the sulfonic acids or their alkali or alkaline earth salts. The reaction is interrupted before all the cellulose passes into solution in the reacting mixture, quickly washed to neutrality, and dried at a low temperature. The diacetates are partially or difficultly soluble in the usual triacetylcellulose solvents, especially chloroform. They have been described by Ost[1] as useful for technical purposes, especially for the preparation of films. Both the cellulose mono- and di-acetates are white, pulverulent and structureless powders, without odor or taste, and when properly prepared are neutral and stable in dry air.

Cellulose Triacetates, so-called "normal triacetates," in general, are those esters produced in the ordinary acetation process working with anhydrous solvents, and low temperatures, continuing the esterification until the cellulose has substantially passed into solution in the reacting mixture. After precipitation by the addition of water, the ester is broken up

1. Zts. ang. Chem. 1906, 19, 993; abst. Chem. Centr. 1906, II, 672; Jahr. Chem. 1905-8, II, 983; Bull. Soc. Chim. 1906, (3), 36, 1053; Wagn. Jahr. 1906, II, 484.

and washed free from acid as soon as possible, to minimize subsequent hydration, and dried at a low heat. The temperature of acetation is governed by the nature of the catalytic agent present, being lowest (for the sake of safety in minimum reduction of the cellulose aggregate) with sulfuric acid as catalyzer, and rising to temperatures of 90°-100° when fused zinc chloride is employed. With cellulose previously dried at 105° until no further loss of weight occurs, and substantially absolute acetic acid and anhydride, the resulting triacetate will be yellowish, hard and horny, of the appearance and color of raw popcorn, soluble in cold chloroform, phenol, aniline, pyridine, or quinoline; partially soluble in tetrachlorethane, more so upon the addition of methyl or ethyl alcohol; partially soluble in acetone and a large number of other solvents; the solubility varying within wide limits, depending upon the nature of the catalyzer employed and the temperature of acetylation, and also being greatly influenced by partial hydration due to moisture in the cellulose employed, the acid or anhydride used, the fineness of subdivision in which the acetate was precipitated and the time required to remove therefrom the catalyzer. The higher acetates, unless thoroughly washed and properly stabilized, tend to slowly decompose to the simpler esters with the liberation of acetic acid and a diminution in solubility. The density of normal cellulose triacetate is 1.2;[1] decomposition temperature about 210°. According to the observations of E. Knoevenagel,[2] stability in solution may be materially increased. Triacetylcellulose is swelled in water to an immeasurable extent, less so in alcohol and other liquids. In the swollen state it is much more receptive to certain solvents, as acetic acid; completely saponified at the ordinary temperature by semi-normal potassium hydroxide in a few hours, and absorbs dyestuffs, such as methylene blue, with speeds roughly proportional to the degree of swelling. The yield of 175% in passing from cellulose to the triacetate theoretically possible is

1. W. Schliemann, Ann. **378**, 366; abst. Chem. Zentr. 1911, **82**, 807; Bull. Soc. Chim. 1911, **10**, 1346; C.A. 1911, **5**, 1276.

2. Zts. ang. Chem. 1911, **24**, 504; abst. J.S.C.I. 1911, **30**, 531; Chem. Ztg. 1911, **35**, 248; C.A. 1912, **6**, 1671.

closely approached on a commercial scale where the various factors in esterification are under proper control. The statement has been made that acetation so conducted as to preserve the original fibrous form of the cellulose leads to a larger yield of triacetate, which is not in accord with the writer's experience. Like the corresponding nitrates, the viscosity is no dependable criterion of the composition. With normal cellulose triacetate the viscosity of a chloroformic solution is an index to the degree of degradation of the cellulose during acetation, the viscosity in a standardized solvent being higher, with minimum change in the cellulose molecule.

From the investigations of de Mosenthal [1] it appears that cellulose mono- and tri-acetate resemble the higher cellulose nitrates in appearing blue when examined miscroscopically by polarized light. W. Schleimann records [2] that normal cellulose triacetate prepared according to the German patent 159524, gave acetic acid of 54.3-60.9%, and an optical rotation of -18° to -14°. The question as to whether H. Ost [3] or A. Eichengruen [4] first drew attention to the fact that normal, maximum cellulose acetylation gives rise to the triacetate, is of no technical importance.

Cellulose Tetracetate. At one time it was considered that what we now call triacetylcellulose was cellulose tetracetate, but it is now generally conceded that the triacetyl derivative represents the maximum degree of cellulose acetylation,[5] the misconception being partly attributable to methods of estimation of acetyl by saponification. While bodies have

1. J.S.C.I. 1907, **26**, 444; abst. Zts. ang. Chem. 1907, **20**, 1970; Chem. Zentr. 1907, II, 687; Jahr. Chem. 1905-8, II, 975; Bull. Soc. Chim. 1907, **2**, 923.

2. Ann. **378**, 366; abst. Chem. Zentr. 1911, **82**, 807; Bull. Soc. Chim. 1911, **10**, 1346; C.A. 1911, **5**, 1276.

3. Zts. ang. Chem. 1906, **19**, 993; 1911, **24**, 1304; abst. Jahr. Chem. 1905-8, II, 983; Bull. Soc. Chim. 1906, (3), **36**, 1056.

4. Zts. ang. Chem. 1911, **24**, 1306; abst. Chem. Zentr. 1911, **82**, II, 750.

5. The reason probably being that during the time required to split off the acyl groups, the cellulose molecule itself suffers disintegration under the influence of the alkali with the result that acidic products are formed. This accounts for the abnormally high saponification numbers, and it was on account of not appreciating this fact that the analytical figures of certain analyses erroneously indicated the presence of a cellulose tetracetate, and pentacetate (Cross and

been obtained which upon saponification gave figures corresponding with a tetracetate, such results are in error from the fact that a variable portion of the alkali is used up in neutralizing decomposition products of the cellulose molecule, in addition to that alkali used in the neutralization of and combination with the acetyl groups.[1] The tetracetates have been described as arising from a far-reaching decomposition of the cellulose complex, and as entirely insoluble in carbon tetrachloride (in which respect it resembles the other acetates), methyl and ethyl alcohol, but soluble in ethyl benzoate, chloroform and glacial acetic acid.

According to a patented process[2] an almost theoretical

Bevan, J.C.S. 1890, **57**, 2; Jahr. Chem. 1890, 2152).

A normal cellulose ester ought upon saponification to regenerate the cellulose and fatty acid as smoothly and quantitatively as is the case with the fats and oils. Should the cellulose molecule have been broken down, however (hydrolyzed), during the progress of the acetylation, we should expect to find a higher saponification value, and the residue should differ widely, both in its chemical nature and in quantity, from the cellulose originally taken. However, in those cases where, from the nature of the acetylizing process, such a decomposition may be anticipated, it will generally be found that an unusual quantity of alkali is used up in the saponification, and that, owing to the high degree of hydrolysis, the yield of regenerated cellulose is much below the theoretical. This cellulose, instead of being indifferent, has acquired strong reducing properties, and when warmed with Fehling's solution causes a precipitation of cuprous oxide.

1. For consecutive statement of this controversy see Chem. Soc. Ann. Rep. 1904, **1**, 69, 70; 1905, **2**, 89; 1906, **3**, 94; 1907, **4**, 89; 1908, **5**, 89. The existence of a tetracetate would not be in accord with the constitutional formula for cellulose proposed (Zeit. Farb. Text. Ind. 1904, **3**, 97, objected to by Cross and Bevan, Ibid. 1904, **3**, 197; answered by Green, Ibid. 1904, **3**, 309, rediscussed by Cross and Bevan, Ibid. 1904, **3**, 441). Cross and Bevan, C.N. 1892, **65**, 77; Jahr. Chem. 1892, 2476; Chem. News, 1892, **66**, 40; Chem. Centr. 1892, II, 401; J.C.S. 1890, 1; 1895, 435, 447. A. Green and A. Perkin have reinvestigated the supposed tetracetate and come to the conclusion that a triacetate is the highest acetyl derivative formed. For cellulose tetracetate and butyrate, see C. Weber, Z. ang. Chem. 1899, 5; Gum. Ztg. 1899, **14**, 49; J. Soc. Dyers, 1899, **15**, 124; C.N. 1899, **80**, 247; Valenta, Phot. Corr. 1901, **38**, 305. Berl and W. Smith (Ber. 1907, **40**, 903; abst. J.C.S. 1907, 1, 289) in their work on acetonitrates could obtain in no case a derivative higher than a triacetate. See D. Law. Chem. Zeit. 1908, **32**, 365, The results of L. Vignon and F. Guerin, C.R. 1900, **131**, 585; Bull. Soc. Chim. 1901, (3), **25**, 139, on acetylated cellulose and oxycellulose pointed to a tetra derivative.

2. E.P. 9998, 1905; Belg. P. 137577, 138462, 1898; D.R.P. 85329, 86368, 1895; abst. Wagn. Jahr. 1896, 685. D.R.P. 105347, 1898; abst. Chem. Centr. 1900, I, 272; Zts. ang. Chem. 1899, **12**,

yield of tetracetate may be obtained by conducting the acetylation in the presence of methyl sulfate, the process being given as follows: 30 parts of cotton are treated in a bath with 70 parts acetic anhydride, 120 glacial acetic acid, and 3 of methyl sulfate until solution is nearly completed. The solution is then filtered, the filtrate precipitated by pouring into a large volume of water, and the acetate neutralized in the usual manner. It is stated that if a solution of this acetate in chloroform be poured upon a glass plate and allowed to remain until the solvent has evaporated, a film of great transparency and tenacity results.

Cellulose Pentacetate has been described[1] as formed when cotton is boiled for 16 hours with acetic anhydride and zinc chloride; melting without decomposition; soluble in acetic acid, from which it is precipitated by water; soluble in boiling nitrobenzene, from which it precipitates in a gelatinous form upon cooling, and dissolving without composition in

1067; Jahr. Chem. 1899, 1290; Wagn. Jahr. 1899, 1064. D.R.P. 120713; Add. to D.R.P. 118538; abst. Chem. Centr. 1901, I, 1219; Zts. ang. Chem. 1901, 14, 574; Jahr. Chem. 1901, 891; Wagn. Jahr. 1901, 612. F.P. 280248, 1898, and First Addition thereto dated Oct. 19, 1898; Luxemb. P. 3302, 3361, 1898; Aust. P. dated Jan. 1, 1899; Feb. 4, 1899; 8165. 1902; Hung. P. dated Aug. 31, 1898; Nov. 8, 1898; the Henckel-Donnersmarck process for cellulose tetracetate is as follows: :720 gm. pure cellulose (preferably prepared from the sulfocarbonate) is mixed with 630 gm. magnesium acetate in a kneading machine with 810 gm. acetyl chloride and 450 gm. glacial acetic acid of at least 99% strength. When the reaction commences 4.5 l. nitrobenzene is added in small portions, the addition being so arranged that about half is added by the time the mass has risen in temperature to 70°. The remaining half is then added in one portion stirred to prevent increase of temperature when the entire mixture is slowly agitated in a mixing machine for three hours. The result is a thin homogeneous solution of the tetracetate rendered opalescent by a small amount of lower acetates and unchanged cellulose. This solution, which has a temperature of about 50°, is poured slowly into 22.5 l. of 95% ethyl alcohol, and the white flocculent precipitate of tetracetate drained and pressed. It is then comminuted without previous drying, boiled with water until last traces of solvent have been dissipated, when dilute hydrochloric acid (equivalent to 2%) is added and heating continued to remove all traces of magnesium salts. The precipitate is then pressed, washed with water to a neutral reaction and dried at a temperature of not to exceed 55°. Of the homologues of nitrobenzene, Henckel-Donnersmarck has used with equal success *o*-nitrotoluene, *p*-nitrotoluene, *o*-nitroethylbenzene, and the nitroxylols and nitrocuminols from isopropylbenzene.

1. Cross and Bevan, J.C.S. 1890, **57**, 2.

cold nitric acid. Not decomposed by boiling with dilute meneral acids.

Cellulose acetates are readily decomposed and easily saponified by dilute solutions of the alkaline hydroxides, especially in the presence of an equal volume of alcohol. Being highly viscous, the cellulose acetates, like the corresponding nitrates, are filtered with difficulty unless greatly diluted. The triacetate is the technically valuable ester, and in commercial methods of preparation it is this ester which is aimed at, whether specifically so stated or not. The triacetate is always contaminated with diacetate, especially in commercial acetation, where from the standpoint of economy the minimum of acetic anhydride to cellulose is generally employed. As with the nitrates, there is no record of a perfectly pure cellulose acetate having been produced, the acetic esters being uncrystallizable, the laws of mass action cannot be applied to the system of acid mixture and cellulose acetate on account of the entire absence of homogeneity. No cellulose acetate has been vaporized or distilled unchanged. Finally, the complexity of the esterizing bath, containing in some instances cellulose, oxycellulose, hydrocellulose and the acetates therefrom, as well as sulfonic and acetosulfonic esters, both in the normal and also the partially hydrated form. Include also as possibilities one or more series of cellulose decomposition products in various stages of hydrolysis and esterification. Systematic experimental studies analogous to the investigations of Lunge and others upon the cellulose nitrates of the influence of the individual constituents o fthe acetating bath upon the final product, permutated for the various acid combinations, and the results plotted on co-ordinate paper, have, as yet, not been published.

Theory of Acetylation. The acetylation of cellulose presents but few theoretical difficulties, is due to the presence of hydroxyl groups in the cellulose molecule, and is facilitated both by the presence of a dehydrating agent, and by an increase in temperature. The acetylation is a bimolecular reaction, the velocity of which may be expressed by the equation:—

$$\frac{DC_1}{dt} :: KC_1C_2$$

C_1 is the concentration of the acid, C_2 that of the alcohols for the time—t. For the esterification itself the following formula applies:

$$\frac{C_1 (C_e - C}{C_1 - C} = C - Ct$$

C_1 signifies the concentration of the acid in the state of equilibrium in the case where an excess of acid over alcohol is present. The concentration of the acid at the time is 0. The state of equilibrium occurs when the acetylated cellulose is dissolved in the reacting liquid, or substantially so. It is heterogeneous when the cotton does not appreciably change its visible form, and homogeneous when the cellulose passes into solution in the acetylating mixture. Heterogeneity always manifests itself where the cotton is acetylated in the presence of a large amount of non-solvent so that the cellulose is inappreciably attacked by the acetic acid and anhydride. The usual inhibitory agents are benzene or carbon tetrachloride. The homogeneous equilibrium takes place in accordance with the law of Guldberg and Waage, and may be expressed in the following terms:

C water — C ester :: R. C. alcohol — C acid

When C alcohol or C acid is present in excess the proportion of ester increases, whereas the presence of an excess of water reduces the quantity of ester. It is, therefore, to bind the water formed in the reaction, and to remove it from the zone of esterification, that energetic dehydrators as sulfuric acid or zinc chloride are indicated.

As compared with nitration, acetylation is a much slower process of esterification. Nitration is an excellent and energetic hydrolyzing medium as well as for esterifying. It is probable that the hydrolyzed cellulose molecule is esterified in *statu nascendi,* and thereby protected against the continued decomposing action of the acids. With cellulose nitrates, of great importance is the fact that the formed ester is insoluble in the nitrating mixture, and as a result is partially withdrawn

from the decomposing influence of the dehydrating agents contained therein, whereas with the corresponding acetic esters, they readily pass into solution in the acetylating mixture because cellulose triacetate dissolves in acetic acid, whereas the cellulose nitrates are insoluble in nitric acid. In opposition, therefore, the conditions of the reaction in the case of the production of the acetylcelluloses are much more unfavorable. The organic acids as acetic acid and acetic anhydride, are substantially devoid of hydrolytic power, and therefore traces of inorganic acids or those compounds which liberate inorganic acids are required to induce incipient hydrolysis. The formation of ester takes place comparatively slowly, so that an energetic hydrolysis is inadvisable on account of a too profound influence upon the esterifying cellulose molecule. Both these circumstances—careful and well regulated hydrolysis and slow uniform acetylation—cause a proportionately extended and often harmful duration to the reaction. Inasmuch as cellulose acetate goes into solution at all stages of the acetylating process, it is difficult to maintain a uniform hydrolysis and therefore to obtain a uniform final product—the first condition in a manufacturing process. This undoubtedly is the explanation of the fact that in operating successively with the same manufacturing process, the solubility of the nitrates and acetates and the viscosity of their solutions fluctuate so greatly and lead to such anomolous results. Similar to the nitric ester, the acetycelluloses show a great variety of qualities dependent upon the number of acetyl groups in the ester, the molecular size of the cellulose, and its state and degree of hydrolysis from the original or normal condition. The variation in solubility of acetates of the same empirical constitution is undoubtedly explainable from the above.

Methods of Manufacture. The process of direct treatment of modified cellulose with acetic anhydride and glacial acetic acid, either with or without the presence of acetyl chloride, is but of historical interest, and, so far as aware, is not used industrially at the present time. There may be said to be but two general classes of preparation methods, and

these are each subdivided into those processes in which the cellulose does or does not pass into solution in the esterizing mixture. The first and earliest of these had to do with the modification of cellulose as a preliminary and distinct treatment as a preparation for acetation, some form of hydrocellulose or modified cellulose being formed as a distinct and separate operation. The earlier processes changed the cellulose directly into hydrocellulose or oxycellulose, or used such modified celluloses as that obtained from precipitation of zinc chloride solutions, recovery from cuproammonium solutions of cellulose, or regeneration from the sulfocarbonates (viscose). Ingenuity in the preparation of these esters has been focused on the subject of the choice of suitable catalyzers which would minimize the reduction of cellulose to bodies of lower molecular weight and hence interfere with the tensile strength of the ester when cast into films. All the methods using hydrocellulose, oxycellulose, cellulose from viscose or mercerized cellulose, gave products of low tensile strength, and at the present time none are commercially produced in this manner. It was George W. Miles, of Boston, Mass., in his U. S. Application 24575, dated July 23, 1900, (allowed Dec. 18, 1900, abandoned, and included in his application dated May 27, 1901), who first disclosed a practical method of preparing chloroform-soluble cellulose acetate directly from fibrous natural cellulose (cotton or tissue paper). At this time the best acetates for film manufacture were those soluble in chloroform. It was Miles, also, who made the next important step, that of partial hydration of the acetated cellulose after formation into the compound of greatest elasticity, strength and flexibility, which he found resulted when the partial hydration was carried to the point of incipient plasticity in cold chloroform, ready plasticity in warm chloroform, and complete solubility in anhydrous acetone, these three solubility results being given at the same time to the product of maximum strength. The partial hydration of acetated cellulose opened up new fields, in that it admitted of the use of solvents of less cost, lower boiling point, greater speed of evaporation, and solvents which were readily obtain-

able in unlimited quantities.[1]

In any method of manufacture the cotton is first bleached and rendered absorbent by removal of fat and wax by scouring, in the same manner and with as great care as exercised in the preparation of the corresponding nitric esters. Certain grades of grass-bleached tissue paper, and the paper used in the manufacture of celluloid, make excellent starting materials for the acetation of cellulose. The speed of acetation is governed by the amount of moisture present, the composition of the acetating bath and the temperature. It is advisable to always artificially dry the cellulose just before acetation, and to introduce it into the acetating bath at room temperature or lower. Where cotton is used, a previous cutting of the cotton to fine powder in a manner similar to that advocated by J. France[2] causes a more uniform acylation with

1. The credit for the discovery of the commercially valuable cellulose acetates, and those of maximum strength, pliability and elasticity as suitable for film formation, has been erroneously ascribed to A. Eichengruen and the Farbenfabriken vorm. F. Bayer & Co., to whom many of his patents have been assigned. In the interests of historical accuracy, the following facts—all public documents available for inspection—are recorded. G. W. Miles was the first to acetate natural cellulose as cotton to a commercially utilizable product, as shown by U. S. Application No. 24575, filed June 28, 1900, and the File Wrapper of which the application forms a part. This eliminated the previous tedious processes of first preparing the cotton for acetylation by a distinct series of operations. Miles was the first to recognize and establish priority of conception by patent application for the process of partial hydration whereby less expensive solvents could be used and the maximum of strength for film formation still be obtained. His German Application, embodying the partial hydration of acetated cellulose, made Sept. 30, 1905, as Application No. M-28289, was, after seven years of continuous litigation, passed by the German Patent Office for issuance, and was then purchased by the litigants and issued by them as D.R.P. 252706 to F. Bayer & Co. This firm had an application covering substantially the same idea, which was applied for on November 29, 1905, as E-20963, and elected by them as an Addition to Miles Application M-28289, which later issued as D.R.P. 252706. The Bayer Co. did not purchase the Miles F.P. 358079, 1905, covering partial hydration in France. It is true that Bayer & Co. was granted a patent in England for the partial hydration of acetated cellulose by precipitating the acetated cellulose, washing to neutrality, drying, and then dissolving the dried cellulose acetate in glacial acetic acid and hydrating. But anyone who has attempted to dissolve normal cellulose acetate in glacial acetic acid will at once appreciate the futility and commercial impossibility of such a method.

2. U.S.P. 420446, 429445, 1890.

the minimum of mechanical effort in the acetating bath, and hence reduces loss of acetic acid and anhydride by vaporization. In any event the cotton should be first passed through a teasing machine to pull the filaments apart and open up all lumps.

Superficial Acetylation of Cellulose. In the improvement of yarns and fabrics before dyeing them, waterproofing textiles and imparting a gloss to cotton cloth, superficial or incomplete acetylization has been proposed. According to the process of L. Lederer[1] the woven cellulose fabric is immersed in acetic anhydride containing 0.5% of sulfuric acid, being left in contact for 10 minutes, or until the exterior has softened and lost its structural form. When the required degree of acetylation has been reached the fabric is withdrawn, washed free from acid and dried, after which the waterproofing may be made more complete by immersing the fabric in a solvent or combination of solvents, passing it through calendar or squeeze rollers to force the softened cellulose acetate into the textile fibers. The solvent is finally completely removed by passage through heated chambers or over a hot drum.

The superficial acetylation of yarn is given in detail under the topic "Dyeing Cellulose Acetate."

Acetylation of Modified Cellulose. Processes for the acetylation of hydrocellulose, oxycellulose, regenerated cellulose from viscose(cellulose sulfocarbonate) and the cellulose cuproammonia processes, are among the earliest attempts to place the acetation of cellulose upon a commercial basis, and to prepare esters of technical importance for use in the industrial arts. These processes, in general, preceded the methods for the esterification of normal or unmodified cellulose, either where the cellulose passed into solution in the reacting mixture, or the acetating bath was so diluted with cellulose acetate non-solvents that the structural form of the original cellulose was substantially conserved. In general, the esters

1. U.S.P. 954810, 1910; abst. J.S.C.I. 1910, **29**, 557; Mon. Sci. 1910, (4), **73**, 135; Chem. Tech. Rep. 1910, **84**, 209. E.P. 11164, 1902; abst. J.S.C.I. 1903, **22**, 646. F.P. 320885, 1902; abst. J.S.C.I. 1903, **22**, 142, 160.

produced from cellulose which differs markedly from the normal do not possess the elasticity, flexibility and tensile strength, as do those esters which have been acetylated by a process which modifies but little the structure and character of the original cellulose aggregate.

Advantage, however, has been taken of the greater reactivity of cellulose obtained by the splitting off of carbon bisulfide from viscose, from cellulose recovered from its cuproammoniacal solutions, or that obtained from cellulose hydrate (mercerized cellulose). The first process of this nature, and the first patented method for the commercial manufacture of acetated derivatives of cellulose, was granted to C. Cross and E. Bevan in 1894.[1] They prepared acetated cellulose from an intermediate product consisting of cellulose and zinc acetate in a state of combination or of intimate mixture. This intermediate product was prepared by taking a form of hydrated cellulose, such as can be obtained from precipitation from the solution of cellulose in zinc chloride or cuprammonium solutions, or from the solution obtained by the treatment of crude cellulose with caustic alkali and carbon bisulfide. The hydrated cellulose obtained in one of the above mentioned ways is thoroughly mixed with a concentrated solution of zinc acetate in the proportion of one or two equivalents of zinc acetate to one equivalent of modified cellulose, the mixture, after thorough incorporation, being dried, and then dehydrated at about 110°. This is then finely powdered and carefully mixed with a definite quantity of acetyl chloride, the temperature being kept under 30° by stirring and cooling. The product of the reaction is treated with water to precipitate the acetate product and remove zinc salts. If unaltered cellulose is to be separated, extraction with chloroform is resorted to, which dissolves the ester, but has no action upon

1. U.S.P. 530826, 1894. E.P. 9676, 1894; abst. J.S.C.I. 1895, 14, 496, 987; Amateur Photog., London, 1899, 80, 146; Brit. Jour. Photog. 1899, 46, 771; Chem. Centr. 1896, 67, 405. D.R.P. 85329, 1894; abst. Chem. Centr. 1896, 67, I, 1119; II, 567; Mon. Sci. 1900, (4), 55, 134; Wagn. Jahr. 1896, 42, 684; Ber. 1896, 29, 312; Jahr. Chem. 1896, 1030. D.R.P. 86368, 1895; being addition to D.R.P. 85329, 1894; abst. Chem. Centr. 1896, 67, II, 567. F.P. 243546, 1894. Belg. P. 113156, 1894.

normal cellulose. The reaction may be inhibited by dilution of the acetyl chloride with chloroform or ethyl acetate. Acetyl chloride as an ingredient of acetating mixtures is rarely, if ever, used at the present time. The following year (1895) these investigators called attention in a practical way to the use of acetic anhydride in small amounts as an adjunct to acetyl chloride in the esterifying mixture,[1] and introduced

1. C. Weber and C. Cross. U.S.P. 632605, 1899. E.P. 22029, 1898; abst. J.S.C.I. 1899, 18, 756. Can. P. 63101, 1899. D.R.P. 112817; abst. Chem. Centr. 1900, II, 510; Zts. ang. Chem. 1900, 13, 773; Jahr. Chem. 1900, 843; Wagn. Jahr. 1900, II, 450. Russ. P. 3264, 1900. Belg. P. 137577, 1898. Dan. P. 2558, 1899. Port. P. 2930, 1899. According to their method, the moist regenerated cellulose is impregnated with the aqueous solution of magnesium and zinc acetates, even penetration being assured by mixing intimately. The mixture is carefully dried, and ground to an impalpable powder. Upon treatment with acetyl chloride and acetic anhydride a reaction takes place which may be represented as follows:

$$2C_6H_{12}O_6 + Mg(C_2H_3O_2)_2 + (CH_3CO)_2O + 2CH_3COCl = 2C_6H_9O_5(C_2H_3O_2)_3 + MgCl_2 + 3H_2O.$$

The equation is calculated upon the supposition that a tri-acetyl derivative is formed. In carrying out the operation 304 parts by weight of the magnesium acetate-cellulose mixture is mixed with 157 parts acetyl chloride and 30-50 parts acetic anhydride, left to stand until the temperature has risen to 50°, when the appearance changes from a moist sandy powder to a semi-fluid mixture. The rise in temperature is controlled by the addition of small amounts of nitrobenzene, incorporating each addition thoroughly, that the temperature may be kept as near 50° as possible. This is important, for with too great a rise in temperature, the cellulose undergoes hydrolysis, and the yield is low and quality poor. On the other hand, a fall in temperature indicates incomplete acetation. Nitrobenzene, being a solvent of the acetate, acts in the capacity of a diluting agent as well as a temperature regulator, and as the produced acetate dissolves, new surfaces of cellulose are exposed to the acetating process. The amount of nitrobenzene is increased as the reaction increases, so that finally an almost complete solution in the solvent results. The viscous solution is then run into alcohol, continually agitated, and the precipitated acetate well washed with water until a neutral reaction is obtained. The nitrobenzol is freed by distilling with steam, the blocks are pressed and finally dried. Purification is effected by solution in dilute phenol and precipitating by running into weak alkali solution. The washed and dried product is then dissolved in chloroform, and is ready for use. Difficulty has been found in regulating the temperature by this method, which Wohl (D.R.P. 139669, 1899; abst. Chem. Centr. 1903, 744; Zts. ang. Chem. 1903, 16, 285; Jahr. Chem. 1903, 1014; Chem. Zts. 1902-3, 610, 673; Wagn. Jahr. 1903, II, 418) sought to overcome by the replacement of the magnesium-zinc acetate by pyridine. It is claimed that the manufacture of cellulose acetate by heating an equimolecular mixture of cellulose and magnesium acetate with two molecules of acetyl chloride, with or without further addition of acetic anhydride, cannot

the use of nitrobenzene, its homologues, epichlorhydrin, dichlorhydrin, as acetation diluents, to moderate, modify or partially control the reaction, and prevent the aggregation of the incompletely acetated product into a solid unworkable mass. The process patented by Henckel-Donnersmarck is similar.[1] Diluents like nitrobenzene prevent a rise of temperature, and enable the acetation process to be more definitely controlled, and hence the ester formed to be more uniform in composition and in physical properties.[2]

L. Lederer,[3] utilizing hydrocellulose prepared according to the process of Girard (see Part One), treated cellulose with 3% sulfuric acid for some minutes, and then heated the acid and cellulose in a closed receptacle to about 70° for a period of three hours. The liquid was then pressed out, the modified cellulose dried and reacted upon with a four-fold quantity of acetic anhydride, the reaction taking place almost immediately with copious evolution of heat. Upon completion of the reaction, the product is precipitated with water, washed to

be carried out on a large scale, owing to the impossibility of controlling the reaction, which, although slow to begin with, invariably proceeds at an increasing rate, causing a rise of temperature fatal to the desired result. Moreover, the final product obtained, if not destroyed, or at least seriously affected by the heat of the reaction, is obtained in the shape of a cake of enormous toughness, the further working of which almost amounts to a practical impossibility.

1. F.P. 280248, 1898. Addition patent of 1898 to F.P. 280248, 1898. D.R.P. 105347; abst. Jahr. Chem. 1899, 1290; 1900, 843; Wagn. Jahr. 1899, 45, 1064; Chem. Ind. 1899, 22, 495; 1900, 23, 449; Zts. ang. Chem. 1899, 12, 1067; Chem. Centr. 1900, 71, I, 272; Mon. Sci. 1900, (4), 55, 134. Wagn. Jahr. 1900, 46, II, 450. D.R.P. 112817 being addition to D.R.P. 105347; abst. Zts. ang. Chem. 1900, 13, 773; Chem. Centr. 1900, 71, II, 510.

2. Norw. P. 7610, 1898. Hung. Pats. dated Aug. 31, 1898. and Nov. 8, 1898. U.S.P. 627031, 1899. E.P. 18283, 1898; abst. J.S.C.I. 1899, 18, 756. Can. P. 62188, 1899. F.P. 282320, 1899. Russ.P. 3378, 1900. Dan.P. 2636, 1899. Luxem.P. 3302, 3361, 7610, 1898. Port.P. 2899, 1899. Belg.P. 138462, 1898, being Add. to Belg.P. 137577.

3. U.S.P. 654988, 1900; abst. Mon. Sci. 1901, (4), 57, 98. E.P. 11749, 1900; abst. J.S.C.I. 1901, 20, 741. D.R.P. 118538, 1899; abst. Chem. Centr. 1901, 72, I, 712; Jahr. Chem. 1901, 891; Chem. Ind. 1901, 24, 330; Mon. Sci. 1901, (4), 57, 213; Zts. ang. Chem. 1901, 14, 345; Wagn. Jahr. 1901, II, 611. D.R.P. 120713, 1900, being Add. to D.R.P. 118538, 1899; abst. Mon. Sci. 1901, (4), 57, 283; Chem. Ind. 1901, 24, 453; Zts. ang. Chem. 1901, 14, 575; Chem. Centr. 1901, 72, 1219. F.P. 301749, 1900; abst. Mon. Sci. 1901, (4), 57, 63; Wagn. Jahr. 1901, II, 611.

neutrality and dried, in which condition it is described as a "gravelly powder soluble in chloroform and nitrobenzene."[1] To further bring the acetylizing process under control, Lederer[2] acetylates in the presence of the cellulose acetate non-solvent, carbon tetrachloride.[3] The hydrocellulose of R. Sthamer,[4] or the oxycellulose of L. Vignon,[5] serves as the starting point for the formation of acetated derivatives according to the protected method of M. Althausse and the Fabrik Chemische Praeperata von Dr. R. Sthamer.[6] In this process,

1. If the hydrocellulose has not been obtained by Girard's process by means of sulfuric acid, but by another process without the aid of sulfuric acid, a small amount of sulfuric acid—about 0.25-0.5% of the weight of the anhydride—must be added to the acetic anhydride for acetylation, because without the presence of sulfuric acid acetylation by means of acetic anhydride does not succeed at a low temperature.

2. E.P. 11749, 1900; abst. J.S.C.I. 1901, **20**, 741. D.R.P. 163316, 1901; abst. Zts. ang. Chem. 1906, **19**, 204; Chem. Centr. 1905, **76**, II, 1301; Mon. Sci. 1906, (4), **64**, 159; Jahr. Chem. 1905-08, 984; Chem. Ind. 1905, **28**, 659. D.R.P. 200916 1901, being addition to D.R.P. 163316, 1901; abst. Mon. Sci. 1911, (5), **74**, 82; Zts. ang. Chem. 1908, **21**, 20, 47; Chem. Zentr. 1908, 738; Chem. Ind. 1908, **31**, 559. F.P. 319848, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Aust.P. 42440, 1909. Cf. W. Walker, U.S.P. 774713, 1904. Also Lederer, Add. of Aug. 22, 1902, to F.P. 319724, 1902; abst. J.S.C.I. 1903, **22**, 563.

3. The following method is illustrative of the process. 10 parts of cellulose is treated with 10 parts glacial acetic acid containing 2.5% by weight of sulfuric acid. After hydrolysis, a mixture of 35 parts each acetic anhydride and carbon tetrachloride is added, and the temperature kept around 30°. The final product possesses the physical structure of the original material.

4. U.S.P. 679204, 1901; abst. Mon. Sci. 1901, (4), **57**, 284. F.P. 304723, 1900; abst. J.S.C.I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1900, (4), **59**, 20. D.R.P. 123121, 1900; abst. J.S.C.I. 1901, **20**, 1133; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901. **72**, 567; Mon. Sci. 1900, (4), **59**, 9; Jahr. Chem. 1901, 892. E.P.19039, 1900; abst. J.S.C.I. 1901, **20**, 926. U.S.P. 679203, 1901; abst. Mon. Sci. 1901, (4), **57**, 284. F.P. 309759, 1901; abst. J.S.C.I. 1902, **21**, 65; Mon. Sci. 1902, (4), **58**, 170. D.R.P. 123122, 1900; abst. J.S.C.I. 1901, **20**, 1133; Mon. Sci. 1902, (4), **58**, 9; Jahr. Chem. 1903, 1014; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, **72**, II, 568.

5. L. Vignon. Comp. rend. 1900, **131**, 509; abst. J.S.C.I. 1900, **19**, 1039. Comp. rend. 1900, **131**, 530; abst. J.C.S. 1900, **78**, i, 629; J.S.C.I. 1900, **19**, 1045. Comp. rend. 1900, **131**, 708; abst. J.S.C.I. 1900, **19**, 1103. Bull. Soc. Chim. 1901, (3), **25**,, 130, 133, 135, 137. L. Vignon and F. Gerin. Comp. rend. 1900, **131**, 588; abst. Jahr. Chem. 1900, 843; J.S.C.I. 1900, **19**, 1103; J.C.S. 1900, **78**, i, 629. Bull. Soc. Chim. 1901, (3), **25**, 139; abst. Jahr. Chem. 1901, 891.

6. U.S.P. 692497, 1902; abst J.S.C.I. 1902, **21**, 362; Mon.

100 parts by weight of hydrocellulose are mixed with about 350 parts by weight of glacial acetic acid and an equal weight of acetyl chloride. The result is an energetic reaction in which hydrochloric acid is split off, and considerable heat developed. As soon as the reaction moderates, a small amount of concentrated sulfuric acid is added to the mixture, the latter thoroughly agitated and then heated to 60°-70°, until the mass has lost its pulpy character and become practically homogeneous. In this stage of acetation the acetylized hydrocellulose is poured into a large volume of cold water, by which means an acetyl derivative is obtained which is soluble in acetone and alcohol, but cannot be precipitated therefrom by the addition of water even upon considerable dilution. This indicates hydration of the acetated product has passed beyond the useful stage of film formation. It is possible to recover the acetylated compound from such a solution by salting out with sodium chloride. Acetylcellulose in this condition is claimed by the patentee to have special technical usefulness for the production of lakes, and as the acetylcellulose in a moist and humid state is very voluminous, a copious precipitate may be obtained even from highly dilute solutions. The lakes thus obtained—in contra-distinction to those precipitated by metallic salts—have the advantage of being absolutely insoluble in water after drying, and of being nearly transparent when applied in a thin layer.

A. Eichengruen and T. Becker and the Farbenfabriken vorm. F. Bayer and Co. have obtained patent protection for a process practically the counterpart of that of Lederer previously described. They act upon hydrocellulose with four parts each of acetic acid and acetic anhydride and one-fourth part of sulfuric acid of 66° Be. strength, and thereby produce an alcohol-soluble ester,[1] in this respect similar to that of

Sci. 1902 (4), **58**, 61. F.P. 308506, 1901; abst. J.S.C.I. 1902, **21**, 64; Mon. Sci. 1902, (4), **58**, 159.

1. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, **60**, (4), 173. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, **75**, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, **60**, 54. It.P. 62042, 1901. See also

Althausse. In a subsequent process[1] the heat of reaction is kept below 50°, and the sulfuric acid reduced from one-fourth part to one-tenth part. A partial hydration is effected—unwittingly or otherwise—by allowing the esterifying mass to remain at rest from 12-24 hours at 40°-45°, when the nearly colorless, thick liquid thus obtained is poured into water, washed and dried. In the dry state it is whitish and voluminous, and soluble in chloroform, epichlorhydrin, nitrobenzene, glacial acetic acid, acetone and pyridine, and insoluble in alcohol, ether, ethyl acetate, amyl acetate or glycerol. Not readily decomposed by cold alkaline carbonates, ammonia or dilute acids, and with difficulty by alkaline hydroxides. The temperature of decomposition is stated as about 250°. In order that the alcohol soluble derivative may be formed in greatest amount, the mixture of 1 part cotton, 4 each of acetic acid and anhydride and 0.1 part sulfuric acid is allowed to stand at from 20°-25°, until, after about 10 hours, the entire mass is transformed into a thick, viscous syrup. The reaction is stopped when the precipitate obtained by diluting a test portion with water contains on the one hand only a small amount of unchanged cellulose, and on the other, is still soluble in hot alcohol. The reaction mass is then mixed with a large amount of water by stirring, and the precipitate obtained, filtered off and pressed. In the wet state it is a whitish voluminous mass, and when dry consists of hard, yellowish lumps. It is soluble in 70% hot alcohol, from which solution a gelatinous mass solidifies upon cooling. An ester of these characteristics is marketed by this firm under the name of Sericose, as a thickening medium in producing the damask effect upon textiles in combination with white pigments. It appears that the acetation takes place in two phases. At first an ester is produced which is soluble in

their D.R. Anm. E-17505, being Addition to D.R.P. 256922; abst. Zts. ang. Chem. 1913, **26**, 700. D.R. Anm. F-28233 of 1909. F-32828 of 1911. F-28111 of 1909. E-14310, 1909. E-14993, 1909. E-15581, 1909, being Addition to E-14998.

1. U.S.P. 790565, 1905; abst. J.S.C.I. 1905. **24**, 686. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, **76**, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-8, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. Aust. P. 31391.

alcohol, but as esterification proceeds the solubility in alcohol diminishes until a product is obtained which refuses to dissolve in absolute ethyl alcohol.[1]

Where viscose is used as the starting point, as in the process of B. Boesch,[2] a less amount of acetic acid and anhydride is required. A satisfactory proportion is 16 parts of cellulose to 1.4 parts magnesium acetate, the former being thoroughly moistened with acetic anhydride and acetyl chloride, to admit of the desired fluidity being maintained during acetylization. As the reaction is usually very energetic, it is best to provide for artificial cooling. The acetated product may be purified[3] by precipitation in petroleum ben-

1. U.S.P. 809935, 1906; abst. J.S.C.I. 1906, **25**, 195; Mon. Sci. 1906, (4), **64**, 120. D.R.P. 185837, 1902, being Add. to D.R.P. 159524; abst. Chem. Ind. 1907, **30**, 313; Chem. Tech. Rep. 1907, **31**, 302; Zts. ang. Chem. 1908, **21**, 269; Chem. Zentr. 1907, **78**, 654; Jahr. Chem. 1905-08, 984. Wagn. Jahr. 1907, II, 403. First Add. 1425, dated Jan. 30, 1903, to F.P. 317007; abst. J.S.C.I. 1903, **22**, 1015. E.P. 7346, 1903; abst. J.S.C.I. 1904, **23**, 337. Aust.P. 32637. E.P. 21628, 1901; F.P. 317007, 1901; Aust.P. 31391; It.P. 62042, 1901, cover the acetylation of cellulose and hydrocellulose by means of acetic acid glacial, acetic anhydride and sulfuric acid, while U.S.P. 734123, 1903; D.R.P. 153350, 1901; covers the acetylation of hydrocellulose only, and U.S.P. 790565, 1905; D.R.P. 159524, covers the acetylation of cellulose only in the manner above described. Next U.S.P. 809935, 1906, is in reality an addition to U.S.P. 790565, as also is D.R.P. 185837, because D.R.P. 185837 and U.S.P. 809935 are additions to D.R.P. 159524 and U.S.P. 790565, which are the corresponding portions of a general patent, and both relate to acetylation of unmodified cellulose only. Furthermore, E.P. 7346, 1903, is an addition to a portion of E.P. 21628, 1901. D.R.P. Anm. Sch. 120, 36144, July 20, 1910, by C. Schwalbe for the manufacture of alcohol soluble cellulose acetates, was abandoned Feb. 15, 1912.

2. U.S.P. 708456, 1902; abst. J.S.C.I. 1902, **21**, 1243.

3. B. Boesch, U.S.P. 708457. 1902; abst. J.S.C.I. 1902, **21**, 1243; Mon Sci. 1903, (4), **60**, 165. In carrying out this invention 3 pounds of an equimolecular mixture of cellulose and magnesium acetate is employed—i. e., a mixture of 1.6 lb. of cellulose, preferably such as is obtained from the sulpho-carbonate of cellulose, with 1.4 of magnesium acetate. To this is added 1.8 lb. of acetyl chloride and 1 lb. of acetic anhydride. This mixture is now placed in a kneading machine provided with a heating or refrigerating jacket and the mass most intimately mixed. As soon as the reaction has gained an appreciable start 1 gal. of nitrobenzene, or equivalent—of its homologues, or epichlorhydrin or dichlorhydrin—is added, at first in very small quantities, adding a further quantity only after the previous addition is absolutely homogeneously incorporated into the acetylizing mixture, the addition as to quantity and time being regulated in such a manner that the last and largest portion of the solvent is added at about the time when the reacting mixture has reached its

zine or benzene, then washing with water and drying. Precipitation in benzine allows of the partial recovery of the esterifying reagents much more readily and cheaply than when water alone is used as the precipitating medium.[1]

By previously digesting cellulose with diluted sulfuric acid, hydrolysis can be carried to a point where the subsequent acetation process is carried on smoothly and can be controlled. Such is the method as worked out by the Badische Anilin & Soda Fabrik.[2] Cellulose is first soaked

temperature maximum, which should not exceed 70°. The agitation of this mixture is then continued for three consecutive hours, when a thinly viscid solution of the acetate is obtained, containing only mere traces of lower acetates or unaltered cellulose. This solution now, while still in the hot state, is strained and then immediately run into 5 gal. of alcohol. The acetate separates out in the form of fine white flakes, which are separated from the mother-liquor by filtration, washed with warm alcohol, which washings are added to the mother-liquor, and then filter-pressed. The product thus obtained is without previous drying broken up and stirred in a very thin pulp with water, which is then heated until all traces of the organic solvent are driven off. The acetate is now again filtered, washed first with warm water slightly acidulated with hydrochloric acid in order to remove the last portions of magnesium salts, and the washings then carried to neutrality with clean warm water. The product is then pressed and dried at a temperature not exceeding 80°.

1. As the reaction is a very energetic one, the container or acetylizing apparatus with the viscose in it is preferably thoroughly chilled before addition of the acetyl chloride and acetic anhydrde. It is also well to previously chill these chemicals. After gradual addition of the cooled acetyl chloride and acetic anhydride the temperature rises very quickly to about 60-70°, and should be kept down as much as possible, at least in the first stage of the process. After addition of the whole quantity of the chemicals and thorough stirring of the mixture, a solvent is added in order to carry the reaction to the end. This solvent may be chloroform, nitrobenzene, nitrotoluene, glacial acetic acid, or others, or a mixture of them. For the preparation of lower acetates the temperature is lowered, less acetyl chloride is taken and acetone used as a solvent. After addition of the solvent, which should be used in a quantity sufficient to dissolve the theoretical amount of cellulose acetate formed—i. e., about ten times the weight of cellulose contained in the viscose originally taken—the container or apparatus is heated for several hours until substantially all the viscose has gone into solution, and during this heating the temperature should not exceed 100°. After conclusion of the reaction the solution of acetate in the particular solvents selected is poured into an equal bulk of ethyl alcohol, which precipitates the acetate. After separation of the precipitated acetate by filtration from the alcoholic mixture containing the solvent, the acetate is washed with fresh alcohol, or boiled with water, until the last traces of alcohol or solvent have been boiled off.

2. U.S.P. 812098, 1906; abst. J.S.C.I. 1906, **25**, 232; Mon. Sci. 1906, (4), **64**, 120. E.P. 24083, 1904; abst. J.S.C.I. 1905, **24**, 1081.

in dilute sulfuric acid, the excess pressed out, and the moist mass then treated with the acetylating agent. However, it is exceedingly difficult to properly control the progress of acetation where moist cellulose is used, the acetation is so energetic, and the rise of temperature so fast, that the invariable result is a darkening of the solution from the formation of subsidiary products and the decomposition of the cellulose. By allowing the acetylation to take place in the presence of an indifferent solvent so that the resulting mixture of solvent, acetic acid and acetic anhydride does not dissolve the acetylated cellulose, the latter can be filtered, or pressed off, and acetic anhydride and glacial acetic acid obtained from the liquid by subsequent distillation.[1] This firm in a subsequent

F.P. 347906, 1904; abst. J.S.C.I. 1905, **24**, 454; Mon. Sci. 1906, (4), **64**, 15; Chem. Ztg. 1905, **29**, 493. D.R.P. 184145, 1904; abst. Chem. Zentr. 1907, **78**, [(5), **11**], 365; Mon. Sci. 1909, (4), **70**, 77; Jahr. Chem. 1905-08, II, 983; Zts. ang. Chem. 1908, **21**, 268; Chem. Ind. 1907, **30**, 238; Wagn. Jahr. 1907, II, 401. D.R.P. 184201, 1904; abst. Zts. ang. Chem. 1908, **21**, 268; Chem. Zentr. 1907, 78, 365; Mon. Sci. 1909, (4), **70**, 77; Jahr. Chem. 1905-08, II, 984; Chem. Ind. 1907, **30**, 257; Wagn. Jahr. 1907, **II**, 402. Aust. P. 35015. Belg. P. 182216, 1905. Swed. P. 20249, 1905. Russ. P. 11492, 1907. See also their E.P. 14042, 1914.

1. The following example illustrates how this invention can be carried into practical effect:

Example 1. Thoroughly soak, in water, 10 parts of cotton (from which any greasy matter has been removed), and then press it until it contains from about 10-20% of water. After loosening this damp cotton introduce it into a mixture of 60 parts of acetic anhydride and 0.3 part of concentrated sulfuric acid. After a short time cool the mixture so as to modify the heat which is evolved, and then digest the mixture at a temperature from 60-70° until a homogeneous thick liquid is obtained. Separate the acetylated cellulose from the reaction mixture by suitable means. Mercerized cellulose can be acetylated in the same way.

Example 2. Soak 10 parts of cotton (from which any greasy matter has been removed) in dilute sulfuric acid (containing about 5% sulfuric acid). Then press the cotton until 2 parts of the dilute sulfuric acid remain. Loosen the cotton press cake so obtained, and introduce it into a mixture of 40 parts acetic anhydride with 40 parts glacial acetic acid. During the reaction heat is evolved, and the mixture should be cooled so that the temperature does not exceed 40°. As soon as a clear solution is obtained, precipitate the acetylated cellulose, wash and dry.

Example 3. Mercerize 100 parts of purified cotton by means of caustic soda, wash it free from alkali and press it until it contains from 10-20% water; then, after loosening, introduce it into a mixture of 400 parts of acetic anhydride, 1.5 parts concentrated sulfuric acid and 1,500 parts of benzene, and gradually heat the whole in a vessel provided with a reflux condenser, to a temperature of

process[1] esterifies hydrocellulose in the presence of bromine or chlorine, iodine monochloride or trichloride, iodine monobromide, or bromine chloride. About 2% of the halogen is found suitable, the temperature being kept around 50°.

H. Peters and H. Cullum have obtained patent protection for a peculiar and involved esterification process,[2] in which the cellulose is hydrolyzed by previous heating with alcohols as glycerol, either with or without the addition of hydrocarbons such as petroleum oils. After the mass is cooled and the adherent oil is removed it is treated with a solution containing formic and palmitic acids, together with a solvent such as methylated spirit. The cellulose is then acetylized in a bath of sulfuric acid, sodium acetate, and acetic anhydride.[3]

from 70-75°, maintained until a test portion of the product is completely soluble in chloroform. The acetylated cotton can be pressed and washed free from the acetylating liquid and then dried. The acetylated cellulose so obtained is soluble in chloroform, aniline, glacial acetic acid, and hot nitrobenzene.

Example 4. Heat 10 parts of dry cotton (from which any greasy matter has been removed) with a mixture of 50 parts of acetic anhydride, 2.5 parts of concentrated sulfuric acid and 150 parts toluene, at a temperature of from 70-80°. As soon as a test portion is soluble in chloroform, the acetylation is complete and the product can be separated off, pressed, washed and dried.

The acetylated cellulose resembles cotton in appearance, but it it brittle and harsh to the touch. It is soluble in chloroform and in acetone and insoluble in water.

Example 5. Soak 100 parts cotton in dilute sulfuric acid (containing 60% H_2SO_4) and then press the cotton until about 10 parts of the dilute acid remain in the press cake. Loosen the cotton so treated and introduce into it a mixture of 300 parts of acetic anhydride and 1,100 parts of benzene. Shake this frequently for a period of about 12 hours, and then heat the whole in a reflux apparatus on the water bath at a temperature of from 60-65° until a test portion is soluble in chloroform. Then press off the acetylated cellulose, remove the excess of acid by means of warm dilute sodium carbonate solution, wash and dry.

1. E.P. 22237, 1911; abst. J.S.C.I. 1912, **31**, 279; C.A. 1913, **7**, 1287; Kunst. 1913, **3**, 175. F.P. 435507, 1911; abst. J.S.C.I. 1912, **31**, 329. Belg. P. 239564, 1911; 248907, 1912. It. P. 73/230/120751 of 1911. D.R.P. Anm. 12o A-21107 of Sept. 24, 1911; abst. Kunst. 1913, **3**, 60.

2. U.S.P. 1008489, 1911; abst. J.S.C.I. 1911, **30**, 1447; Mon. Sci. 1912, **77**, 163. U.S.P. 1008557, 1911; abst. J.S.C.I. 1911, **30**, 1447. E.P. 16000, 1911; abst. J.S.C.I. 1912, **31**, 637; C.A. 1913, **7**, 252; Kunst. 1913, **3**, 175. E.P. 822, 1912; J.S.C.I. 1912, **31**, 637. E.P. 2859, 1912. See also their F.P. 432747, 1911; abst. Mon. Sci.

3. Example. 1 kilogram of raw cellulose is heated for about

L. Grote[1] prepares a binding-medium for use in making plastic materials by treating cellulose or substances containing cellulose with dilute sulfuric acid in the cold or at a moderately low temperature. The mixture is brought into a granular or flocculent state by decantation or filtration, and afterwards dried, the binding-medium being formed by dissolving the dried mass in a suitable solvent, such as glacial acetic acid (with or without phenol), acetone, acetic ether, acetic anhydride, naphthalene or benzaldehyde. Magnesium oxide or magnesium carbonate is added to facilitate the setting of the medium, and an adhesive, quick drying binding-medium obtained by adding a solution of glue or gelatine and glycerol. Glacial acetic acid or benzaldehyde may be added to assist the action of the sulfuric acid in the first stage of the process and in the example given the cellulose product is dissolved in a mixture of glacial acetic acid, acetic anhydride, acetone, carbon tetrachloride, and glycerol.

L. Landsberg[2] heats 1 part of hydrocellulose or oxycellulose with about 4 parts of acetic anhydride containing 1% of orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid or a smaller amount of phosphoric anhydride (phosphorus pentoxide), on a water bath with constant stirring at from 40°-50°, as long as the consistency permits, the result

4 hours in glycerin, or petroleum oil, or any other oil. With petroleum oil the temperature is maintained at about 40°, with other oils it is kept below the boiling point. After the mass has been allowed to cool, the oil is pressed out thoroughly and the cellulose dried. The cellulose is then put into a bath consisting of 10 grams methylated spirit, 50 grams formic acid and 20 grams palmitic acid. The cellulose is steeped or pressed until it has been thoroughly impregnated by the liquid. After 4 hours the whole mass is put into a bath consisting of 2-3.5 liters glacial acetic acid or other condensing agent; 3 liters acetic anhydride; 100 grams sulfuric acid; 10 grams sodium acetate. This mass must be cooled down and always kept below 50°. After about 10 hours the whole is poured into methylated spirit containing about 30 grams ammonium carbonate per liter. The cellulose product is kept in this for about 6 hours, when the liquid is filtered off and the product immersed in water containing 30 grams ammonium carbonate per liter. It forms very strong, non-inflammable films when dried.

1. E.P. 23728, 1912; abst. C.A. 1914, **8**, 1346.

2. E.P. 4886, 1902; abst. J.S.C.I. 1903, **22**, 315. F.P. 316500. 1901; abst. J.S.C.I. 1902, **21**, 719; abst. Mon. Sci. 1903, (4), **59**, 53. Aust. P. 17456, 1902. D.R. Anm. L.-15737.

being a tough, gelatinous product. Upon completion of the reaction, the acetylized product is precipitated in the usual manner, washed and dried.[1]

Commercial Manufacture of Partially Hydrated, Acetone-Soluble Cellulose Acetate. The following method, covered by the Miles patents[2] is sufficiently detailed to enable those skilled in the art to uniformly and uninterruptedly produce hydrolyzed cellulose acetate of maximum strength and flexibility for film formation. To 100 parts by weight of bone dry,[3] scoured[4] cellulose,[5] and preferably bleached,[6] add in

1. As initial material, the following oxycellulose products are recommended by the patentee as particularly useful for esterification by this method. (a) That formed from cellulose by treatment with potassium chlorate and hydrochloric acid (Vignon, Compt. rend. 1897, **125**, 448); (b) that obtained from the action of nitric acid upon cellulose (Cross and Bevan, J.C.S. 1883, **43**, 22; Tromp de Haas and Tollens, Ann. 1895, **286**, 296; Faber and Tollens, Ber. 1889, **32**, 2590, and Nastukoff, Ber. 1891, **34**, 3589); (c) oxycellulose obtained by the action of bromine and calcium carbonate on cellulose (Faber and Tollens, Ber. 1889, **32**, 2591).

2. U.S.P. 733729, 1903; Can. P. 90848, 1905. U.S.P. 838350, 1906; Reissue thereon, 12637, 1907; abst. Mon. Sci. 1907, (4), **66**, 116, 159; J.S.C.I. 1906, **25**, 195; 1907, **26**, 165. E.P. 19330, 1905; F.P. 358079, 1905; Hung. P. 35866, 1905; Belg. P. 187308. 1905; Aust. P. 41461, 1909; Can. P. 103045; It. P. No. 97, vol. 215, 1905; D.R.P. Anm. M.-28289, 1905; issued as D.R.P. 252706, 1905, to Farbenfabriken vorm. F. Bayer & Co.; abst. Zts. ang. Chem. 1912, **25**, 2621; Chem. Ind. 1912, **35**, 770; Kunst. 1913, **3**, 35; C.A. 1913, 7, 550. See also F. Bayer & Co., D. R. Anm. 12o, E.-20963, 1905; being addition to D.R.P. 252706; abst. J.S.C.I. 1903, **22**, 961; 1906, **25**, 865.

3. In cellulose, the moisture present exerts a marked influence upon the speed and difficulty in controlling the acetation, air dry cellulose (containing 5-7% moisture) acetating much more rapidly than when the moisture has been reduced to 1-2% by drying, i. e., so-called bone dry cellulose. With increase of moisture, the heat of reaction is higher and danger of decomposition greater, especially where sulfuric acid is used as the dehydrating or "contact" agent. With increase of moisture, more vigorous stirring is required at the commencement of the acetation to prevent localized acetylation and preheating, and to completely disintegrate the cellulose that it may be uniformly acted upon before the major portion of the acetic anhydride has gone into combination, and thus lowered the acetic acid content of the acetating mixture to a point where it is unable to dissolve the partially acted upon cellulose. Where air dry cellulose is used, additional acetic anhydride should be added to compensate for the moisture present. Where one is acetating small amounts of cellulose, it makes but little difference as to the amount of moisture contained therein, especially where an excess of acetic anhydride is used, and the temperature is artificially kept down.

4. Although glacial acetic acid and acetic anhydride are excel-

one portion[1] a mixture of acetic anhydride equivalent to 270-310 grams of absolute anhydride,[2] 390-410 grams glacial

lent solvents of chlorophyl and vegetable fats, it is always advisable to scour cellulose intended for acetation, using the same care as bestowed upon that intended for nitration and use in smokeless powder.

5. In general, tissue paper and ramie acetate more slowly than cellulose, and probably give more dependable results. Ramie, especially, is difficult of acetation, but produces films, when properly hydrated, of great strength and suppleness. Cotton acetates more readily, and where the cotton has been previously disintegrated as according to the patented process of J. France (U.S.P. 420445, 420 447, 1890; E.P. 20973, 1890; J.S.C.I. 1889, 8, 303; 1890, 9, 821), much less energy is required to reduce the acetating mass to a uniform pulp. White birch or poplar wood pulp acetates rapidly and with less uniformity. With ramie and tissue paper, a larger bulk of acetating fluid is required than with cotton and wood pulp, yet when thoroughly saturated with anhydride, grass bleached tissue paper free from glaze or filler, acetates very uniformly. With wood pulp the temperature must be kept well reduced at all stages or brittle films will result from the partially hydrated ester. With ramie and tissue, about 15% more glacial acetic acid is required for facility in handling over the amount necessary for disintegrated cellulose (cotton dust or wood pulp).

6. To produce colorless films, it is requisite that the cellulose be bleached before acetation, and also advisable to replace the water used in hydration with a concentrated hydrogen dioxide solution as described. With tissue paper, grass bleached is preferable to chlorine bleached, in that the former appears to give stronger and more tenuous films.

1. In some processes it is advocated to leave the cellulose in contact with the acetic acid and sulfuric acid for some hours before the acetic anhydride is added. The longer the cellulose has been in contact with the acetic and sulfuric acids before the acetic anhydride is added, the quicker and more energetic will be the reaction, the more difficult to control, and the greater liability of weakening the strength of the hydrated acetate from overheating at this point of the acylation. These difficulties are increased in proportion to the moisture present in the cellulose. For instance, allowing the acetic and sulfuric acids to remain at room temperature upon an air dry cellulose, the addition of cold acetic anhydride thereto would probably produce such a rapid reaction that the temperature would rise too fast to be controllable and an inferior and weak acetate would result. To produce esters of predetermined solubilities and maximum strength in film form, it is necessary that the several steps in the process be accomplished gradually and remain under complete control at all times. It is more discreet to use bone dry cellulose, and to add the acetating constituents at a temperature under 40° to the cellulose at one time. Under these conditions no apparent action is observable for some minutes, which gives the manipulator an opportunity to thoroughly disintegrate the cellulose and intimately intermingle the acetating fluid therewith.

2. Commercial acetic anhydride ranges in strength from 85-95% absolute anhydride, equivalent by titration to 115-117% absolute acetic acid. The gravity of acetic anhydride is no criterion of

acetic acid,[1] and 3-5 cc. commercial sulfuric acid of 66° Be. strength.[2] The cellulose in 5 kilo batches[3] is placed in a 40-liter stoneware or porcelain crock, and the acetating mixture poured on, the temperature of the acetating fluid being its strength. Acetic anhydride being the most expensive constituent of the acetating mixture, it is obvious that in commercial work the minimum of anhydride used is continually sought. Probably 2.4 volumes anhydride to 1 gram cellulose is the minimum limit to which it is safe to go. Whether the cellulose is acetated in closed or open containers has much influence in governing the minimum amount of anhydride required.

1. Of at least 99.5% strength, glacial acetic acid of the U. S. and British Pharmacopeas, signifying acetic acid of 99% strength or over. The equivalent of 390-410 grams 99.5% acetic acid in cc. is 368-388 at 15°, and this must be regarded as a minimum amount.

2. Miles (U.S.P. 838350, 1906, Reissue 12637, 1907), has acetated cellulose with 0.25% sulfuric acid by weight. Where a small amount of sulfuric acid and a small excess of anhydride is used, the acetylation temperature can be kept higher, with safety, than where larger amounts of sulfuric acid are employed. If the temperature is not kept at 50° or above where the acetic anhydride is at the minimum or deficient, the mixture may become stiff and heavy and finally gelatinize. In the latter condition further addition of acetic anhydride or acetic acid has but little appreciable effect, and it is not possible to produce therefrom by proper hydration films of maximum strength. Raising the temperature does not overcome tendency to gelatinization, because there is insufficient anhydride and sulfuric acid to continue the reaction to the triacetate stage. The greater the amount of sulfuric acid used in the acetating mixture, the less the viscosity of the acetating mixture, greater care must be exercised to guard against undue rise in temperature, for with a higher temperature and more sulfuric acid, the acetated cellulose is prone to break down, giving a hydrated product whose acetone or chloroform-alcohol film has decreased tensile strength. Where fuming sulfuric acid is employed, about 60% of the equivalent of sulfuric acid 66° Be. is used, or about 2% calculated on the weight of cellulose. There is no advantage to be gained by using the fuming acid over 66° Be. strength. Most dependable results are to be obtained by keeping the amount of sulfuric acid used and the temperature of reaction both low, and allowing the reaction to occupy a longer period of time.

3. This being about the maximum amount which can be handled by manual labor alone, especially if fibrous cellulose such as Massasoit cotton or tissue paper be used. In working with such a large bulk, the reaction temperature must be kept down until the entire mass is thoroughly disintegrated, otherwise local preheating will take place, and interfere with the uniformity of the final product. In the commercial manufacture of cellulose acetate, a porcelain lined dough mixer containing ammonia refrigeration jacket, combined with facilities for introducing hot water or steam by means of coils, enables the temperature of reaction to be kept under control. A platinum couple or other automatic temperature recording device is essential, and should be attached to the mixer so as to be readily visible at all times. The mixer should be fitted with an air-tight cover to minimize loss of anhydride.

preferably under 40°.[1] The cellulose is continually stirred and broken up with a sharp-edged porcelain spatula, until the combined stirring and reacting mixture gradually transforms the cellulose into a white, non-transparent, pasty mass.[2] During this time the temperature, for the best results, should not be allowed to exceed 50°, artificial refrigeration being resorted to if necessary. When the cellulose has become entirely disintegrated and homogeneous, the heat of reaction should be allowed to rise to the maximum temperature,[3] still with constant stirring. When the reaction temperature begins to fall[4] the container should be placed in warm water and a temperature of 50°-55° maintained in the acetating pot. The mass will rapidly become transparent and decrease in viscosity, and when the cellulose has apparently entirely passed into solution,[5] forming a heavy, nearly transparent.

1. If the cellulose has not all been uniformly worked into the reacting mixture, as the strength of the acetating fluid diminishes from combination with the cellulose, it becomes almost impossible to bring the partially unacted-upon cellulose into solution, the tendency being to have translucent lumps in the finished acetating mixture just prior to hydration. If not filtered out after hydration and before precipitation, these give insoluble material not dissolved by any cellulose acetate solvents. The first noticeable activity of the acetating mixture upon the cellulose is when the latter begins to lose its elasticity. It is necessary to pour the acetating mixture over the cellulose rather than to immerse the latter in the former, for the volume of fluid is kept so small the cellulose would not be completely wetted.

2. When the acetic acid, acetic anhydride and sulfuric acid is mixed, there is a noticeable and continuous evolution of gas, which is of no consequence.

3. The maximum temperature where cotton is acetated by substantially the formula given is about 65°, and depends upon how thoroughly the cellulose has been disintegrated, how nearly transparent the mass is, and the amount of sulfuric acid originally employed.

4. From the viscosity, degree of transparency and general appearance of the acetating mixture at this point, is determined the amount and length of time artificial heat is to be applied. If the mass is very viscous and of marked opalescence, a higher temperature is required than where the fluidity is greater and the mass more nearly transparent. At a temperature of 50°, with frequent agitation of the mass, there is little danger of injurious decomposition.

5. Normal cellulose triacetate is completely soluble in glacial acetic acid and chloroform, but insoluble in pure acetone, and is technically the most useful ester, because partially hydrated cellulose triacetate is completely soluble in pure acetone and gives the strongest and most flexible films. Therefore, in the acetation of

light brown mass, free from but insignificant amounts of unacted upon fibers, a test portion is removed, precipitated in a large bulk of water, washed until neutral, and dried, when it should completely dissolve in alcohol-free chloroform with or without heat, and be nearly or quite insoluble in acetone of 99.5% strength or better.[1] At this point the acetated mixture is ready for partial hydration, as indicated by the appearance and solubility tests in chloroform and acetone. A mixture of 60-65 cc. water and 60 cc. glacial acetic acid[2] per 100 grams cellulose taken is made, and this added slowly from a burette to the acetating mixture, meanwhile stirring

cellulose, the process should be carried to that stage where cellulose triacetate predominates, in order that the partially hydrated acetone-soluble films shall have maximum strength. This is equivalent to saying that the reaction must continue to complete solubility in acetic acid (the reaction mixture), before hydration is attempted. In order to insure this, sufficient acetic anhydride must be present to affect the transformation into triacetate, and the heat must be maintained at a point to prevent gelatinization. Increase of anhydride aids in the solution of the acetate in the reacting mixture, insures acetation at lower temperatures, and proneness to gelatinization is correspondingly obviated. Any lumps present cannot be cloth filtered out, due to the action of the acetating mixture upon the cloth. After hydration, however, they may be thus removed without danger, the addition of the hydrating mixture preventing further acetation. It may sometimes be difficult to tell whether all the cellulose has passed into solution due to the presence of insoluble fibres. By taking a small sample out, adding acetic anhydride and warming, the solution will clear if there was a deficiency of anhydride, otherwise not.

1. The best non-hydrated cellulose acetate, and hence the most desirable for hydration, is, in the author's experience, obtained when an excess of acetic anhydride (320-350 grams per 100 gm. cellulose) is used, and the temperature kept below 40°. The period of acetation may require 2 or 3 days, and the hydration an equal length of time, but the hydrated film obtained from pure acetone solutions has great strength and flexibility. Where low temperatures are maintained, there must be a considerable excess of anhydride present in order to carry on and complete the reaction in the absence of heat. Low temperature acetations invariably result in very viscous solutions.

2. The amount of water required will depend upon the original amount of anhydride used, and the amount lost by evaporation during the subsequent acetating process, for a portion of the water is consumed in transforming the anhydride into acetic acid. When acetating in an open container, for each 100 gm. cellulose, for 3 volumes of acetic anhydride, experience has shown that 62-65 cc. water is the correct amount, while with 4 volumes anhydride, from 72-75 cc. water is required. The object of the acetic acid is simply as a diluent to enable the water to more readily permeate the acetated mass. Ten per cent. sulfuric acid can be used, but acetic acid

the mass vigorously and continuously.[1] When the hydrating is preferable on account of the ease of manipulation. If the anhydride is lowered to the minimum safe limit, i. e., 2.4 volumes, 45-48 cc. water will be found sufficient. If normal cellulose acetate be precipitated out, dried and then redissolved in acetic acid as advocated by Farbenfabriken vorm. F. Bayer and Co. (E.P. 24067, 1906; F.P. 371447, 1906; abst. J.S.C.I. 1907, 26, 340, 1213), only 20-25 cc. water will be required per 100 gm. original cellulose. This, however, is a very tedious process due to the difficult solubility in acetic acid of cellulose acetate when dried, and the process offers no advantages. In general, irrespective of how the ester is produced, best cellulose acetate is not obtained unless the reacting mass is substantially clear before hydration, irrespective of the time of acetation. The water of hydration may be replaced by a 25 volume solution of hydrogen dioxide, which is mixed with the acetic acid and incorporated with the acetated mass. The effect of the bleaching power of the peroxide is immediately noticeable by a bleaching of the solution, which continues to become lighter color during the entire hydration period. Hydration tends to decrease the solubility in pure chloroform and at first to increase the solubility in pure acetone, and after a while in acetone carrying water. As hydration continues or increases, solubility in chloroform diminishes until a partial solubility represented by the word plasticity is evident. At this stage the hydrated acetate is entirely soluble in 99.5% acetone, or a little weaker, and makes the toughest and most pliable films. Hydration continued beyond this point is shown by a decreased plasticity in hot chloroform, until the hydrated acetate becomes brittle in chloroform, becoming a fine powder with little or no coherence. The solubility in acetone from the point of continued hydation from the product plastic in hot chloroform and at the same time soluble in absolute acetone, shows itself by increased amounts of water which it is necessary to add to the acetone in order to cause it to dissolve the acetate. This may continue until the unduly hydrated acetate will dissolve best in acetone of say 20% water. Such films prepared therefrom are worthless. Therefore, granting the cellulose has been properly acetated, the hydration portion of the process —for best results—should be carried only to that intermediate stage distinguished by plasticity in hot chloroform and solubility in anhydrous acetone.

1. It is advisable to allow the acetated cellulose solution to cool somewhat before the hydration mixture is added, especially where a considerable excess of acetic anhydride has been used, due to the heat developed by the union of water and anhydride. If the hydration is accomplished by a mixture of acetic acid and water and the original amount of sulfuric acid added as esterifying agent was also low, this precaution loses its value. The addition of water will often raise the temperature of the entire mass to 70° or higher. Irrespective of whether the hydrating mixture is water alone, water and acetic acid or water and sulfuric acid, it should be added very slowly from a burette or seperatory funnel, with constant and vigorous stirring, that the hydration may be thoroughly and equitably carried on. The hydration of a 5-kilo batch of cellulose might with profit require an hour. Probably the proper point to interrupt hydration is when the hydrated acetate is just softened by chloroform at 50-60°, but the plasticity must be sufficiently separated from solubility so the insoluble mass does not stick to the fingers. When

mixture has all been incorporated[1] so gradually that no precipitation ensues or lumps appear, the pot is placed in a temperature of 40°-50° for 12-16 hours, and until a small sample removed, precipitated, washed and dried, is found plastic in warm[2] chloroform and entirely soluble in pure

plastic in cold chloroform, the acetation should have been carried a little further before hydration. This applies especially to cellulose acetates made at temperatures of 60-70°, for when the acetate has been made at temperatures around 40°, it is practically as good for film formation when plastic in cold as in hot chloroform. Often when the acetate has been hydrated too far, upon drying after hydration, the mass feels sticky and can be lumped together in the hand. Inasmuch as 2% ethyl alcohol will cause a chloroform to dissolve hydrated cellulose acetate, in which otherwise it would be insoluble, it is evident that in testing partially hydrated cellulose acetate for solubility in, or plasticity with chloroform, the latter must be free from absolute or other strength ethyl alcohol.

1. Knoll & Co. (D.R.P. 274260, 1912; abst. J.S.C.I. 1914, 33, 746) precipitate acetylcellulose by means of concentrated saline solutions, such as sodium acetate.

2. The progress of hydration cannot be followed by the appearance of the hydrating mass. However, precipitated normal or unhydrated cellulose acetate is tough, hard, horny and translucent, and cannot be broken by the force of the thumb and forefinger. As hydration proceeds, the precipitated mass becomes more opaque, whiter, and much softer to the feel, until when the desired degree of hydration has been reached, there is found a mass which can readily be powdered between the thumb and forefinger and is pure white in appearance. Continued hydration causes the hydrated acetate upon precipitation to disintegrate to so fine a mass as to become milky-looking in the water, at which stage much is lost during the washing processes in obtaining neutrality. The feeling therefore of the precipitated hydrated cellulose acetate is an accurate criterion of the degree of hydration. As hydration proceeds, the perfect solubility in chloroform of cellulose triacetate gradually decreases until entire insolubility in cold chloroform results. The next step is that form of incipient solubility designated by the word plasticity, from which it quickly merges into complete insolubility as hydration continues. With acetone the reverse is the case. The chloroform-soluble non-hydrated acetate is insoluble in pure acetone or nearly so. As hydration progresses, solubility in acetone increases to a point in which the partially hydrated ester is completely soluble in cold absolute acetone. From this point continued hydration results in the formation of bodies which are soluble in acetone containing increasing amounts of water, it being possible to produce a partially hydrated cellulose acetate completely soluble in acetone containing 20% of water. However, from the point of complete solubility in absolute acetone, continued hydration results in films of less value, until the films obtainable from an acetone carrying 20% of water are friable and worthless.

When the normal acetate, therefore, is made by a process in which the maximum acetating temperature has not been allowed to rise much above 40°, the films obtained from the partially hydrated acetate in chloroform, and the still further hydrated ester in ace-

acetone.[1] The entire acetated cellulose is then precipitated as a voluminous white mass by slowly pouring into cold water, washed quickly [2] until neutral, and dried at a tempera-

tone, should both be good. When acetated at temperatures around 60-70°, films from hot chloroform solutions of the partially hydrated acetate are inferior. However, if the hydrated acetate is plastic in hot chloroform, the films from absolute acetone probably will be good. When cellulose is acetated at 60-70° there is great difference in the films as to whether they are soluble or plastic only in chloroform, films from the modification plastic in chloroform being much the superior.

1. The following generalizations indicate the progress and degree of hydration of the acetated cellulose when a test sample is examined. If the partially hydrated cellulose acetate is:

(1) Soluble in cold chloroform and insoluble in pure acetone—insufficiently hydrated.

(2) Soluble in both chloroform and acetone—insufficiently hydrated, but hydrated more so than (1).

(3) Insoluble in chloroform, soluble in acetone—properly hydrated for films of maximum strength and flexibility.

(4) Insoluble in chloroform and insoluble in acetone—an impossibility if the cellulose had passed into solution in the reacting mixture, for any cellulose acetate soluble in glacial acetic acid is at the same time either soluble in pure chloroform or pure acetone. Moreover, any hydrated acetate plastic in warm chloroform will dissolve in that chloroform by the addition of a small amount of ethyl alcohol, and at the same time be soluble in acetone.

The same cellulose acetated by the same formula, if the temperature is allowed to rise to 65-70°, upon hydration will give rise to an ester which is obtained by precipitation in a very fine and soft powder, hard to wash, but easy to dissolve when dry. If the acetating and hydrating temperature was not allowed to rise above 49°, the hydrated acetate precipitates out in strings or flakes as a fibrous mass, porous and easy to wash. It, however, dissolves less readily. It is a noticeable fact that, whereas unmodified acetated cellulose is soluble in chloroform, and the addition of small amounts of alcohol will precipitate the ester, whereas modified or partially hydrated acetated cellulose which is on the border line between solubility and insolubility in chloroform, the addition of alcohol to such a solution will cause the ester to immediately pass into solution. The acetone-soluble form of acetated cellulose is readily dissolved by acetone oil and tetrachlorethane, but not by pentachlorethane, although partially gelatinized by it. Solubility in pentachlorethane is increased by the addition of small amounts of crystalline hexachlorethane. This form of cellulose acetate, and the cellulose acetates in general, differ from the corresponding cellulose nitrates, in their greater antagonism to castor oil, so that castor oil in sufficient quantities to induce elasticity has not as yet been able to have been added to cellulose acetate. Although castor oil is soluble in acetone and acetylene tetrachloride, yet when, say, an acetylene tetrachloride solution of castor oil is added to an acetylene tetrachloride solution of cellulose acetate, the latter precipitates out, if enough castor oil has been added to induce plasticity and flexibility.

2. After precipitating the hydrated acetate, it should be washed free from acid as quickly as possible, so the acid contained

ture of 35°-40°. Thus prepared the partially hydrated cellulose acetate is a white, fibrous mass, devoid of taste or smell, soluble in formic or acetic acids with some difficulty, readily soluble in tetrachlorethane, pure acetone, chloroform containing a small amount of ethyl alcohol, less soluble in ethyl acetate, nitrobenzene and pyridine, and insoluble in water, alcohol, amyl alcohol, amyl acetate, carbon tetrachloride, benzine, benzene, toluene or xylene. It is plastic in hot chloroform, in which the plasticity should be sufficiently distinct from solubility so the plastic mass will not stick to the fingers. Soluble in 70% hot ethyl alcohol from which it gelatinizes on cooling. Plastic in 95% ethyl alcohol at 100° (i. e., under pressure). Plastic in glycerol at 125°. Soluble in a mixture of equal olumes of hot ethyl alcohol and benzene, from which it is thrown out in the cold. The yield from 100 grams of cellulose will vary between 130 and 145 grams of partially hydrated cellulose acetate.

If the sulfuric acid is replaced by anhydrous zinc chloride as the condensing medium, acetation and hydration can both be conducted at a higher temperature (around 65°) without danger of decomposition of the cellulose.

In the method of A. Wohl [1] the cellulose is first steeped in glacial acetic acid, or other organic liquid miscible with water, such as formic acid or acetone, then pressed until the weight is about 1.2 times the original weight, the moist fiber being then introduced into the anhydrous esterifying agent. It is stated that in this way uniformity of penetration and reaction is insured by the elimination of the hygroscopic moisture and the substitution of a miscible liquid. If desired, a small amount of catalytic agent may be added to the acetic acid. It is a fact that although glacial acetic acid has apparently no effect upon cotton cellulose, yet such cellulose will more readily esterify if it be first treated with glacial acetic

in the acetate will not continue to hydrolyze. The acetic acid must be removed very carefully, for films containing minute amounts of free acid lose a considerable amount of their strength and become brittle upon storing.

1. E.P. 20527, 1912; abst. J.S.C.I. 1913, **32**, 823. F.P. 448072, 1912; abst. J.S.C.I. 1913, **32**, 420; Kunst. 1913, **3**, 195; Mon. Sci. 1914, **80**, 3.

acid at ordinary room temperature, the ease of subsequent acetation increasing with the length of time the cellulose has previously stood in contact with the glacial acetic acid.

Other Partial Hydration Processes. In addition to the typical Miles partial hydration process of acetone-soluble cellulose acetate manufacture various subsequent modifications have been proposed. The Farbenfabriken vorm. F. Bayer and Co.[1] soak the dry acetylcellulose in a mixture of 500 parts of concentrated hydrochloric acid of about 25° Be. strength and 2500 parts of water, until a test portion taken out, washed free from acid and dried, is found to dissolve in acetone. The impracticability of the process is evident from the fact that in the acetation of cellulose, it is first precipitated out and dried, and afterwards treated in the solid state with a hydrolyzing medium. In contradistinction, the Miles process hydrolyzes while in solution in the acetylating mixture, whereby not only several processes are eliminated, but the dissolved acetylated cellulose hydrolyzes much more readily in the dissolved state than when it has been precipitated and dried, the drying causing it to harden and indurate. The patentees continue the process until the cellulose ester becomes soluble in dichlorhydrin, epichlorhydrin, glacial acetic acid and in a mixture of 20 parts by weight of alcohol and 80 parts by weight of acetic ester(the particular ester not being specified). The hydrochloric acid may be replaced by other acids, such as oxalic, citric, lactic, tartaric, monochloracetic, dilute nitric or phosphoric.

H. Danzer[2] introduces water in the hydrolyzing mixture by indirect production, using the water normally eliminated when a primary alcohol is esterified with an acid. With alcohol and acetic acid the products would be, of course, ethyl acetate and water. He introduces 300 parts of alcohol into an esterifying mixture of 100 parts of cellulose and sufficient

1. E.P. 24067, 1906; abst. J.S.C.I. 1907, **26**, 1213; F.P. 371447, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 79; Chem. Tech. Rep. 1907, **31**, 149. Consult Jacquet, E.P. 29882, 1913; D.R. Anm. H.-57941, 1912, R. Hoemberg.

2. F.P. 428554, 1910; abst. J.S.C.I. 1911, **30**, 1155; Chem. Tech. Rep. 1911, **35**, 576; C.A. 1912, **6**, 2169; Mon. Sci. 1913, **78**, 125.

acetic acid and anhydride, and on warming, the water "in the nascent condition" brings about the special hydrolysis claimed in the patent. Eliminating the question of patent circumlocution, it is difficult to see the reason for producing for this purpose water in such an expensive manner.

The Chemische Fabrik von Heyden[1] claim to produce chloroform-insoluble and acetone-soluble—and this is at the point of partial hydration where the acetated product forms films of maximum tenuity and tensile strength—by treating cellulose acetate solutions containing 56-62% of combined acetic acid with 50-80% sulfuric acid. The time necessary for the treatment varies from 1-6 hours, and until the acetic acid content of the treated ester is reduced to 52-54% of combined acid. With such a large proportion of concentrated acid it is difficult to see how the hydration process may be controlled. If the temperature be reduced, gelatinization of the entire mass is prone to occur, and the solubility seriously interfered with.

Knoll and Co. take cellulose acetate prepared by a process which yields a product insoluble in acetone, and convert it into a modification soluble in that medium by heating either the finished substance, preferably dissolved in acetic acid—or else the direct product of the reaction—with catalyzers such as neutral or acid salts of sulfuric acid, chlorides or nitrates, in the presence of not over one part of water to one part of cellulose acetates. When the direct product of the acetylizing reaction is employed, the excess of acetic anhydride should be destroyed by the addition of water, alcohol or glycerol. In such cases the catalyzer which serves for the acetylation is also equally applicable for the subsequent partial hydration. In the examples cited, methylamine sulfate or bisulfate or

1. F.P. 438649, 1912; abst. J.S.C.I. 1912, **31**, 534; Kunst. 1912, **2**, 439. D.R. Anm. W.-30500, 1911, being addition to D.R. Anm. W.-30036, on the preparation of hydrocellulose esters of organic acids; refused. See F. Bayer & Co., D.R.P. 252661, 1912, Add. to D.R.P. 245575; abst. Ztg. ang. Chem. 1912, **25**, 1034, 2381; Chem. Ztg. 1912, **34**, 1174; Chem. Tech. Rep. 1912, **36**, 248, 610; Chem. Ind. 1912, **35**, 775; Chem. Zentr. 1912, **83**, 1709. Also Act. Ges. f. Anilinfabr., E.P. 1156, 1913; D.R. Anm. A.-23352, Jan. 15, 1913.

zinc chloride is used. With the latter an elevated temperature of hydrolysis is necessary for best results.[1]

Or,[2] the cellulose acetate may be alternately treated in the solid form, as threads, bands or films, by sprinkling it with a solution of benzene, sulfoacetic acid and acetic anhydride, and continuing the action until the ester has become insoluble in chloroform. When the catalyzer is added to a solution of cellulose acetate in glacial acetic acid, the mass, at first gelatinous, gradually separates in a solid insoluble form.

The process of L. Lederer[3] offers but little that is new. He acetylates cellulose with acetic acid, acetic anhydride and sulfuric acid in the usual manner and produces gelatinous solutions which are further treated with sulfuric acid. He adds 20 parts each of glacial acetic acid and acetic anhydride to 5 parts of cotton and 1 part by weight of sulfuric acid, acetylates at 20-25°, and then stirs in 20 parts of water, leaves for a few days, finally bringing the reaction to a close by the addition of 1.5 parts of sodium acetate in 6 parts of water. In the author's experience, it would be impossible to add so large an amount of water as specified without precipitation of the acetylated cellulose in such a viscous and insoluble form as to render hydrolysis practically impossible without the subsequent aid of heat and a large volume of acetic anhydride. Certainly the amount of water advocated—four times the weight of cotton employed—is unduly excessive.

1. F.P. 453835, 1913; J.S.C.I. 1913, **32**, 785. For the method of manufacturing cellulose ester solutions by Plinatus, see E.P. 16940, 1913. According to F.P. 452374, 1912, and Add. P. 17104 of 1913 thereto, amines as aniline, toluidine and the xylidines, or benzene and ethyl alcohol and toluene and methyl alcohol are efficient for transforming acetone insoluble into acetone soluble cellulose acetates.

2. Knoll & Co., E.P. 8990, 1912; J.S.C.I. 1913, **32**, 823. F.P. 442512, 1912; Chem. Tech. Rep. 1912, **36**, 693; C.A. 1913, **7**, 1288; J.S.C.I. 1912, **31**, 917; Belg. P. 224950, 1912; Kunst. 1912, **2**, 300. D.R. Anm. K.-47775, April 28, 1911. D. R. Anm. 12o, K.-50333, 1913; Kunst. 1913, **3**, 279.

3. F.P. 441864, 1912; abst. J.S.C.I. 1912, **31**, 916; Mon. Sci. 1913, **78**, 141. E.P. 7687, 1912; J.S.C.I. 1913, **32**, 483; C.A. 1913, **7**, 3025. F.P. 455117, 1913; Kunst. 1913, **3**, 439; abst. Mon. Sci. 1914, **80**, 11; J.S.C.I. 1913, **32**, 865. E.P. 3849, 1913; abst. J.S.C.I. 1913, **32**, 940. See also Verein. f. Chem. Industrie in Mainz, E.P. 9266, 1914.

The Verein fur Chem. Ind. in Mainz [1] heat chloroform-soluble cellulose acetate in solution, in the presence of small amounts of water and in the absence of substances of pronounced hydrolytic action, until the ester becomes soluble in ethyl acetate. Continuation of the treatment results in the formation of an ester soluble in acetone. As an example, 50 parts of cellulose acetate are dissolved and heated at 100° with 500 parts of 95% acetic acid for about 20 hours. The water present in the acetic acid, in the above formula, is sufficient to induce the desired partial hydration. Similar effects are said to be produced with 90% acetic acid at 105-110°, or in a shorter time with 90% formic acid at 100-110°. The latter temperature, however, is above the boiling point of formic acid. If the reaction product of the acetylation is treated direct, and without isolation of the ester, it is necessary to neutralize the catalytic agent, e. g. by the addition of sodium acetate or ammonia, and to add sufficient water to decompose the acetic anhydride. This last step in practice, however, is unnecessary.

In another method [2] cellulose acetates soluble in chloroform and insoluble in, or but little affected, by acetone, and which contain 55-59% of combined acetic acid, are heated with aromatic amines, e. g., aniline, at temperatures ranging from 90° to 220°. A modification of the acetate gradually takes place, so that in the first stage it retains its solubility in chloroform but becomes soluble in acetone and in ethyl acetate. On further heating, the solubility of the substance in chloroform and ethyl acetate decreases, but it remains soluble in acetone and in a mixture of benzene and alcohol. At still later stages the substance becomes soluble in aqueous acetone or alcohol. These changes may be interrupted at any desired stage of solubility; they take place more rapidly if a small quantity of a strong acid or the amine salt of such an acid be added to the aniline or other amine employed Example: 20 parts of cellulose acetate are heated with 200

1. F.P. 455117, 1913; abst. C.A. 1914, **8**, 573; J.S.C.I. 1913, **32**, 865; E.P. 3849, 19008, 1913.

2. Chem. Fab. auf Actien, (vorm. E. Schering), and A. Loose. F.P. 452374, 1912; J.S.C.I. 1913, **32**, 652, 784. F.P. 450890, 1912.

parts of aniline at 190°. After 4-6 hours the product becomes soluble in acetone. If 0.2 part of aniline phosphate be added, the same result is obtained in 1 hour.

Or,[1] the solubility may be modified through a series of changes by heating them with aromatic amines, either in presence of salts soluble in the aromatic amines or capable of combining with them to form salts, or in presence of compounds which react with the aromatic amines to form amino-salts. The reaction may be carried out under pressure with or without diluting agents. Example: 10 parts of cellulose acetate are boiled under a reflux condenser with 100 parts of aniline with the addition of 0.2 part of diethylamine hydrochloride or quinoline sulfate, or 0.1 part of ethylenediamine hydrochloride or 0.3 part of zinc chloride, the time of boiling ranging from 2 to 3 hours. The cellulose acetate may be digested in the autoclave with aniline and benzene or alcohol under a high pressure.

According to the Verein f. Chemische Industrie in Mainz[2] cellulose acetates soluble in ethyl acetate to a very viscous solution may be prepared by heating a solution of cellulose acetate soluble in chloroform or acetone, the solution containing water, but no hydrolytically acting substance. The heating is carried out at a high temperature and is continued until a sample dissolves in ethyl acetate. In examples given, the acetate is heated with 9-95% acetic or formic acids to temperatures of 100-110°. Or the crude mass of the acetylating process may be treated directly, but in this case the contact substance must be rendered harmless by a suitable addition. E. g., the crude mass is diluted with 50% acetic acid to bring the acetic acid present to 90% strength, and sodium acetate added to neutralize the action of the sulfuric acid used as contact agent, and the heating continued at 105-110%; or if zinc chloride is used as contact agent, ammonia is added with the glacial acetic acid.

1. Chem. Fab. auf Actien, (vorm. E. Schering), and A. Loose. First Addition dated Jan. 16, 1913, to F.P. 452374, 1912; abst. J.S.C.I. 1913, **32**, 784. See also D.R. Anm. 12o, C.-21994, of 1912.

2. E.P. 3849, 1913; abst. C.A. 1914, **8**, 573, 2620.

W. Parkin and A. Williams [1] first treat cellulose with 4.5 times its weight of glacial acetic acid and 2.8 times its weight of acetic anhydride, together with 10-15% sulfuric acid (calculated on the cellulose). The ingredients are directed to be mixed and left at the ordinary atmospheric temperature for 12-14 hours.[2] Then 25% (calculated on cellulose) of nitric acid diluted with three times its volume of water is added and the entire mass mixed (if possible). After standing for another 12-14 hours it is precipitated with water, washed and dried. The base finally obtained is claimed to be soluble in chloroform, glacial acetic acid and acetone, and to be especially useful as a celluloid substitute when mixed with camphor or camphor substitute such as triphenyl phosphate, trinaphthyl phosphate, or similarly-acting body.

Knoll & Co. have quite recently [3] proposed to produce acetone-soluble acetylcellulose from the acetone-insoluble insufficiently hydrated form by means of the application of heat alone. They prepare cellulose acetate solutions which are viscous in acetone by treating solutions of acetates insoluble in acetone with sulfates in the presence of small quantities of water.[4] Either neutral or acid sulfates are said to be applicable, methylamine sulfate being especially valuable. Or,[5] similar acetates may be prepared by the use of a chloride or nitrate in place of the sulfate. The use of

1. E.P. 26657, 1909; abst. J.S.C.I. 1910, **29**, 1152. F.P. 421010, 1910; abst. J.S.C.I. 1911, **30**, 416.

2. With the proportion of sulfuric acid to cotton, and the amounts of acetic acid and anhydride as stated, the acetylating mixture left at ordinary room temperature would solidify to a jelly-like and opaque mass, the cotton refusing to pass substantially into solution. In the acetation of cellulose with the mixture as above stated, practical experience has shown that a temperature higher than that of the ordinary room is necessary to cause the esterification to proceed to the transition stage claimed by the patentees as "anhydrous cellulose acetate."

3. Belg. P. 253353, 1913; abst. Kunst. 1913, **3**, 355. E.P. 16905. 1913. See also Knoll & Co., D.R. Anm. K.-48490, of July 14, 1911; D.R.P. 255704, 1911; abst. Kunst. 1913, **3**, 40; Chem. Zentr. 1913, **84**, 482. D.R. Anm. K.-52025, of July 17, 1912; K.-52789, of Oct. 9, 1912; abst. Kunst. 1913, **3**, 200.

4. E.P. 2491, 1913; F.P. 453835, 1913; abst. C.A. 1914, **8**, 2482; J.S.C.I. 1913, **32**, 785; 1914, **33**, 308. D.R.P. 273706, 1911; abst. Kunst. 1914, **4**, 179.

5. E.P. 4353, 1913; abst. C.A. 1914, **8**, 2804; J.S.C.I. 1914, **33**, 349. D.R.P. 274260, 1912; abst. Kunst. 1914, **4**, 234.

alkali metal chlorides is excluded, and in the case of the organic bases, the amine must be capable of being acidilized by organic acid anhydrides. According to examples given, cellulose is acetylized with the aid of zinc chloride, ammonium chloride, cupric chloride or ammonium nitrate, and after the addition of a small quantity of water, the action is continued until the product shows the desired solubility in acetone.

According to the process of the Chem. Fabrik auf Aktien (vorm. E. Schering) [1] the solubility of cellulose acetates may be modified by heating them with an aromatic amine with or without addition of a small quantity of an acid or a salt of the amine. By heating in this manner cellulose acetates soluble in chloroform and insoluble in acetone and acetic ester, products are obtained which are soluble in all these solvents; on further heating the products become soluble in hot mixtures of benzene and ethyl alcohol or toluene and methyl alcohol, and on heating for a still longer period acetates soluble in diluted alcohol and diluted acetone are obtained. Suitable amines are aniline, its homologues and alkyl derivatives.

Where the solubility of cellulose acetates is modified by partial hydrolysis by the action of water or a dilute acid, the treatment is liable to be irregular owing to the precipitation of a portion of the ester by the aqueous reagent. According to V. Pauthonier [2] this irregularity is prevented by carrying out the hydrolysis by the addition of an anhydrous agent which is a solvent of the constituents of the mixture and which is capable of combining with the liberated acetic anhydride, while furnishing a hydroxyl group to produce the hydrolysis. Suitable agents are acetone, phenol and chloral hydrate; when necessary, these may be diluted with glacial acetic acid.

Other bodies containing hydroxyl besides water can be used for the hydration of acetated cellulose. Ethyl alcohol, phenol, hydroxy acids as lactic acid, glycol and glycerol are examples of mono-, di-, and trihydric alcohols which are

1. E.P. 27227, 1912; abst. C.A. 1914, **8**, 1668.
2. F.P. 466009, 1913; abst. J.S.C.I. 1914, **33**, 589; Kunst. 1914, **4**, 235.

suitable, dynamite glycerol being especially so. Those cellulose acetates which are prepared without visible change in structural form may be hydrated by means of alcohol, water being of no value on account of its immiscibility with benzene or carbon tetrachloride. By varying the nature and amount of OH body used, and the period of hydration, products may be isolated soluble in alcohol-benzine, alcohol-benzene, alcohol-chloroform, water-acetone, alcohol-ethyl ether, alcohol-benzyl alcohol, and similar combinations.[1]

In F. P. 455117 are claimed new fatty acid esters which possess the valuable property of dissolving in ethyl acetate, forming clear, viscid solutions. The process for the manufacture of these esters consists in heating to about 90-100° the chloroform, or acetone-soluble cellulose esters in aqueous solution in the absence of any agent exercising a hydrolysing action, until a sample, after having been precipitated by water and dried gives a clear solution with acetic ester. It is requisite for a proper success of the reaction that the esters remain in solution during the entire course of the reaction. In carrying out the process, the dry acid esters of cellulose may be used, or the reaction product in the form as it is obtained directly from the known methods of acetylation. In the latter instance care must be taken that the contact substance remaining in the acetylation mass is rendered harmless by suitable additions. For instance, 50 parts chloroform-soluble celluloseacetate is dissolved in 500 parts acetic acid (95%) at a temperature of 100° and the solution maintained at this temperature until the sample is soluble in acetic ester, which is usually the case after about 20 hours. (90% acetic acid may also be used, in which case the reacting mixture is heated to 105°-110°.) Or, an acetylation mass, like the one obtained after the process described in German Patent No. 159524, namely, by carefully allowing 800 parts acetic anhydride, 600 parts glacial acetic acid and 5 parts sulfuric acid to act upon 200 parts cotton, is mixed with diluted acetic

1. A series of patents for solubility variation by hydration has been granted to H. Dreyfus, E.P. 20975, 20976, 1911; 20852, 21376, 1912; abst. C.A. 1913, 7, 890; 1914, 8, 1010. Swiss P. 63586, 1911; abst. C.A. 1914, 8, 252.

acid of 50% in such quantities as necessary to reduce the acetic acid present in the mixture to 95% strength. This would mean in the particular case mentioned here that about 285 parts of diluted acetic caid of 50% will have to be added. Furthermore, 10 parts of anhydrous sodium acetate are added to the mixture and the whole heated to 105°-110° until a sample dissolves in acetic ester, forming a clear solution. This process can also be used with advantage to produce the known cellulose esters, soluble in chloroform, acetone, mixtures of chloroform and alcohol, and mixtures of chloroform and acetic ester. It is distinguished from the previously known processes by the fact that high temperatures for the reaction are employed during any desired length of time without producing a detrimental side effect by hydrolytic splitting of the cellulose molecule. This is of great technical importance, because the mixtures are, at high temperature, very mobile and consequently can be readily moved by pumps, and are easily filtered and also precipitated by water, which is not the case with the thick liquid obtained by previously known processes. For instance the acetylization product, obtained from 800 parts acetic acid anhydrid, 600 parts glacial acetic acid, 5 parts sulfuric acid and 200 parts cotton is mixed with 285 parts acetic acid of 50% strength and 10 parts of sodium acetate added. The mixture is heated to 100°-110° until a sample dissolves in acetone, forming a clear solution.

Similar to the Miles partial hydration process is the saponification method patented by H. Mork,[1] in which hydration is induced by a reduction in acetic acid content by removal

1. U.S.P. 1061771, 1913; abst. C.A. 1913, **7**, 2707; J.S.C.I. 1913, **32**, 597. F.P. 416752, 1910; abst. J.S.C.I. 1910, **29**, 1871. E.P. 20672, 1910; abst. J.S.C.I. 1911, **30**, 354; C.A. 1911, **5**, 2947. See also his U. S. Applications, 637857, 637858, 1911. If a chloroform-soluble, non-hydrated, acetone-insoluble cellulose acetate be taken, dissolved in absolute acetone, and a little dry sodium carbonate added, the cellulose acetate in 12-24 hours will pass into solution, thus showing that the sodium carbonate hydrolyzes cellulose acetate from the form insoluble in acetone to that modification completely soluble. In U.S.P. 1074092, 1913; abst. J.S.C.I. 1913, 32, 975; Mon. Sci. 1914, **80**, 11; Kunst. 1914, **4**, 157; C.A. 1913, **7**, 3839; H. Mork applies the hydrolysis as described in U.S.P. 1061771, 1913, to sheets, films and filaments. See also Safety Celluloid Co. F.P. 458263, 1913; abst. C.A. 1914, **8**, 2251.

from a higher ester of acetylcellulose a portion of the combined acetic acid by means of alkaline saponifying agents. The partial removal of the combined acetic acid by saponification may be effected in several ways, as by the application of the usual saponifying chemicals as sodium or potassium hydroxide, ammonia or alkali or alkaline earth carbonates. This saponification may be applied to acetated cellulose in which the fibrous nature of the cellulose has been substantially conserved, or it may be applied directly to the neutralized ester obtained from precipitation from the esterifying mixture.

The length of time of saponification, the amount and strength of alkali hydroxide or carbonate, and the temperature during hydrolysis, determines the acetic acid content of the final product and its solubility in named solvents. According to statements of the patentee, treatment with aqueous ammonia of sp. gr. 0.9 for 16 hours at 15°-20°, hydrolysis can reach the stage in which the product is insoluble in acetone, alcohol, ether, acetylene tetrachloride, chloroform and glacial acetic acid, but is soluble in phenol. However, if such acetylated cellulose is boiled for 2 hours with a 0.4% aqueous solution of NaOH the product becomes insoluble also in phenol.

In the process of the Internationale Celluloseester Ges.[1] for preparing neutral cellulose acetate solutions, the acid acetylated mixtures, obtained by the usual method, are diluted with an organic liquid or mixture of liquids, which is not capable of dissolving the dry acetate which is precipitated; on addition of a suitable base, the acid is precipitated in the form of a salt and filtered off, whilst the cellulose acetate remains in solution. These solutions are capable of being gelatinised, even when dilute.

In the manufacture of acetated hydrocellulose as described by the Mitteilungen d. Techn. Gewerbemuseum Wien [2] cotton is saturated with sulfuric acid of 4% strength, and pressed and dried in the air at ordinary temperatures. The dry cellulose is

1. D.R.P. 260984, 1912; abst. Kunst. 1912, **2**, 300; **3**, 273; J.S.C.I. 1913, **32**, 748; C.A. 1913, **7**, 3228.

2. Wagn. Jahr. 1905, II, 192.

heated in an asbestos lined tin box for 8 hours to 70°. The mass is then broken up, washed with much water and the ash neutralized with soda. Ater washing once more the cotton is pressed, dried in the air and finely powdered. To 150 gm of this hydrocellulose powder are added 500 gm. pure acetic acid anhydride to which has been added 1.5 gm. pyrophosphoric acid, the operation being carried out in an enamelled vessel and heated to 50°. The temperature rises gradually first and towards the last reaches 98°. Ater three hours a homogeneous mass is obtained, which is diluted with much water and washed neutral to litmus and dried at a low temperature.

Acetation with Sulfuric Acid Containing Catalyzers—Lead chamber crystals form the basis of the patented process of H. Dreyfus,[1] the nitrosyl sulfate being brought into contact with the cellulose, acetic anhydride or acetyl chloride at ordinary temperature, or up to 70°. If it is desired to preserve the structure of the starting material, various diluents as benzine, petroleum ether, carbon tetrachloride or other non-solvent may be added to the esterifying mixture. When the ester is precipitated into water, the lead chamber crystals may be neutralized by the addition of various bases or basic materials, sodium formate being especially applicable. If a large quantity of nitrosylsulfate is added to the acetylating mixture the action is too vigorous, so that the solubility in acetone is increased to that stage in which the acetated cellulose dissolves readily in acetone containing various amounts of water, in which condition the acetated cellulose does not produce films of maximum strength and flexibility. Cellulose acetate produced in the above manner may be made soluble in chloroform, acetylene tetrachloride, formic acid, glacial acetic acid, propionic acid, nitrobenzene, pyridine, phenol and acetone, either alone or in mixtures.

V. Pauthonier[2] introduces sulfuric acid in the guise of liberating sulforicinoleic acid in the acetating mixture to induce "suppleness and plasticity" to the finished ester. He

1. F.P. 413671, 1910; abst. J.S.C.I. 1910, **29**, 1101; Mon. Sci. 1918, **78**, 78; Chem. Tech. Rep. 1910, **84**, 250. See E.P. 8676, 1913.
2. E.P. 27102, 1909; abst. J.S.C.I. 1911, **30**, 19; Chem. Tech. Rep. 1911, **35**, 59. F.P. 409465, 1909; abst. J.S.C.I. 1910, **29**, 751.

reacts on cellulose with sulfo-fatty acid and acetic anhydride, the finished product being described as white and soft to the touch; not pulverulent and of somewhat the appearance of wood shavings or certain lichens, which, when collected in a mass assumes a spongy consistency. The products—which are readily soluble in chloroform, glacial acetic acid and acetone—may be obtained, for instance, by treating 162 gms. of dry cotton with 460 gms. of acetic anhydride, 600-700 gms. of acetic acid (to dilute the otherwise too viscous solution and to moderate the reaction), when 5-50 gms. of sodium sulforicinate (alizarin assistant or turkey red oil) are finally added, together with sufficient sulfuric acid to liberate the sulforicinic acid.[1] The reaction is complete when a sample removed, washed and dried, is found soluble in acetone.

Ammonium bisulfate is the catalyzer claimed by the Societe L'Oyonnithe as especially applicable for the formation of cellulose esters,[2] the cellulose being treated with a mixture of glacial acetic acid, acetic anhydride and ammonium bisulfate at a temperature in excess of 50°. The interaction between the bisulfate and glacial acetic acid liberates sufficient sulfuric acid to admit of esterification being properly carried on.[3]

A. Wohl finds (and truly) [4] that all kinds of cellulose or hydrocellulose can readily be esterified within a considerable

1. To avoid rise of temperature, and to facilitate the reaction, the patentees advise mixing the glacial acetic acid, the sulfuric acid, and about a third of the anhydride with the cellulose, then add the balance of anhydride and the sulforicinate only after the reaction has commenced and easy mixing is possible. It is claimed that the acetylated cellulose esters are not mixtures of ricinoleate of cellulose, sulfate of cellulose and acetated cellulose, but an "intimate combination." Sodium sulforicinoleate may be made by cooling 1 k. castor oil and adding to it gradually and in small portions at a time 250 gms. sulfuric acid of 66° Be. strength, also cooled. The mixture is constantly stirred, kept cool, washed with water upon completion of reaction, then neutralized.

2. F.P. 427265, 1911; abst. J.S.C.I. 1911, **30**, 1051; Chem. Tech. Rep. 1911, **35**, 481; Mon. Sci. 1913, **78**, 123. Hung. Appl. O.-674, 1912. Aust. P. 29b, A.-1787, 1912; Kunst. 1912, **2**, 460.

3. To obtain this variety of acetated cellulose, 400 parts glacial acetic acid, 300 parts acetic anhydride, 20 parts of dry, finely powdered ammonium bisulfate is next introduced, and finally 100 parts of cellulose, the temperature, meanwhile, being kept under 50°.

4. D.R.P. 139669, 1903; abst. Jahr. Chem. 1903, 1014; Chem. Ind. 1903, **26**, 167; Wagn. Jahr. 1903, **49**, II, 418; Zts. ang. Chem. 1903, **16**, 285; Chem. Centr. 1903, I, 744. D.R.P. 243581, 1908;

range of temperature, provided the time of reaction and the amount of sulfuric acid used as catalyst are properly regulated. When treating cellulose containing no ash(tissue paper being a typical example) 0.2% or less of sulfuric acid is sufficient, whereas with ordinary filter paper about 0.4% is necessary, and correspondingly larger amounts of sulfuric acid where the ash is higher. With these amounts of sulfuric acid, the whole of the cellulose can be converted into acetate by acetic anhydride in one or two hours time at a temperature of 100°-120°. The author, however, believes such a high temperature will not admit of keeping the esterification process under proper control, even with as low amounts of sulfuric acid as 0.2%, if film material is desired of the final acetated cellulose. At a temperature of 100° or over, there will always be considerable reduction of the cellulose as evidenced by the darkening of the esterifying mixture, and the thinness of the solution toward the end of the reaction. At such high temperatures, when the cellulose begins to pass into solution in the esterizing mixture, it is extremely difficult to keep the process under proper surveillance.

In order to obviate the use of the expensive acetic anhydride, it has been proposed to produce the required acetic anhydride in the acetylizing mixture.[1] To this end the action of phosgene generated by the action of sulfur trioxide upon carbon tetrachloride is allowed to act upon acetic acid, the reaction proceeding as indicated in the following equation:[2]

$$2\,SO_3 + CCl_4 = S_2Cl_2O_5 + COCl_2$$

$$2CH_3CO_2H + COCl_2 = (CH_3CO)_2O + 2HCl + CO_2$$

The process is carried out by treating 10 parts of cellu-

abst. J.S.C.I. 1912, **31**, 381; Chem. Abst. 1912, **6**, 2316; Chem. Tech. Rep. 1912, **86**, 196; Zts. ang. Chem. 1912, **25**, 654; Chem. Ind. 1912, **35**, 190; Chem. Zentr. 1912, **83**, 695. E.P. 20527, 1912; abst. C.A. 1914, **8**, 1010. See D.R. Anm. 30500; being Addition to W.-30436. W.-38008, of Aug. 31, 1911; abst. Kunst. 1913, **3**, 180.

1. Societe anonyme L'Oyonnaxienne, F.P. 432751, 1911; abst. J.S.C.I. 1912, **31**, 123. See also P. Ekstroem, Swed. P. 33546, 1911; abst. C.A. 1913, **7**, 289. P. Engelskirchen, D.R.P. 255441, 1911; abst. C.A. 1913, **7**, 1587.

2. For detailed information concerning pyrosulfuryl chloride and chlorosulfonic acids, see Sertuerner, Gilberts Ann. 1822, **72**,

lose and 200 parts of acetic acid with 25 parts of oleum (fuming sulfuric acid) of 130° strength in the presence of 100 parts of carbon tetrachloride, the whole being heated under a reflux condenser at a temperature of about 65° for about an hour. After the acetylation is complete the residual reagent is then distilled off under a pressure of 100 mm. Finally the cellulose acetate is precipitated by water, washed and recovered.[1]

The use of various sulfuric acid esters, sulfinic and sulfonic acid bodies have been made the basis of patent protection as catalyzers in the esterification of cellulose, but as has been pointed out by C. Schwalbe [2] and others, the efficiency of

109. Dobereiner, Gilberts Ann. 1822, **72**, 331. Gmelin, Gilberts Ann. 1823, **73**, 209. Rose, Pogg. Ann. 1836, **38**, 117. Rosenstiehl, Compt. rend. 1861, **53**, 658; Jahr. Chem. 1861, 120; Rep. chim. pur. 1861, (4), 60. Rose, Ann. chim. phys. 1838, **44**, 291; Bers. Jahr. 1840, **19**, 201. Rose, Pogg. Ann. 1839, **46**, 167. Regnault, Compt. rend. 1838, **7**, 895. Rose, Pogg. Ann. 1841, **52**, 57; 1852, **85**, 510. A. Williamson, Proc. Roy. Soc. 1854, **7**, 11; Phil. Mag. 1854, (4), **7**, 365; J.C.S. 1855, **7**, 180; J. prakt. Chem. 1854, **62**, 377; Ann. 1854, **92**, 242. R. Williamson, J.C.S. 1858, **10**, 97; J. prakt. Chem. 1858, **73**, 73. Schiff, Ann. 1857, **102**, 114. Persoz and Bloch, Compt. rend. 1849, **28**, 86. Baumstark, Ann. 1866, **140**, 75. Williams, J.C.S. 1869, **22**, 304; Zts. f. Chem. 1869, **12**, 665. Schuetzenberger, Compt. rend. 1869, **69**, 352; Jahr. Chem. 1869, 209; Ann. 1870, **154**, 375. Armstrong, J. prakt. Chem. 1870, **109**, 244; Ber. 1869, **2**, 712; 1870, **3**, 730. Prudhomme, Compt. rend. 1870, **70**, 1137; Ann. chim. Pharm. 1870, 156, 342. Michaelis, Jena. Zeitschr. 1871, **6**, 235; Zts. f. Chem. 1871, **7**, 149. Carius, Ann. 1858, **106**, 307. Mitteilung, Ann. 1873, **170**, 1. Geuther, Ber. 1872, **5**, 924. Mueller, Ber. 1873, **6**, 227. Clausnitzer, Ber. 1878, **11**, 2007. Thorpe, J.C.S. 1880, **37**, 358. Ogier, Compt. rend. 1882, **94**, 82. Mitteilung, Compt. rend. 1882, **94**, 217. Konowalow, Compt. rend. 1882, **95**, 1284. Ogier, Compt. rend. 1883, **96**, 66. Heumann and Kochlin, Ber. 1883, **16**, 479. Konowalow, Ber. 1883, **16**, 602; Compt. rend. 1883, **96**, 1146. Erdmann, Ber. 1893, **26**, 1990. Moureau, Bull. Soc. Chim. 1894, (3), **11**, 767. Prandtl and Borinski, Zts. ang. Chem. 1909, **62**, 24.

1. Distillation of acetic acid and anhydride in the presence of fuming sulfuric acid, and in the presence of acetylated cellulose in solution, must, of necessity, be prejudicial to the acetylating product, from the continued action of the catalyzer during the time and heat of the distillation. For exhaustive article on pyrosulfuryl chloride and chlorosulfonic acid, see C. Sanger and C. Sanger and E. Riegel, Zts. ang. Chem. 1912, **76**, 79; abst. J.S.C.I. 1912, **31**, 1681; Chem. Zentr. 1912, II, 683; Bull. Soc. Chim. 1912, **12**, 1418; J.C.S. 1912, **102**, ii, 752; C.A. 1912, **6**, 1721.

2. Zts. ang. Chem. 1910, **23**, 433; abst. Jahr. Chem. 1910, I, 648; Chem. Zentr. 1910, I, 1964; Bull. Soc. Chim. 1910, (4), **8**, 694; J.C.S. 1910, **98**, i, 224.

these are all due to the rapidity or completeness with which they eliminate or split off sulfuric acid during some stage of the process of acetation. The first of these methods to be patented is the process of H. Mork, A. Little and W. Walker,[1] in which difficulties of former condensing agents as sulfuric acid, zinc chloride, zinc or magnesium acetates or iodine, may be obviated by causing the reaction with cellulose to take place in the presence of an aromatic sulfonic acid, as phenol sulfonic acid or naphthol-sulfonic acid. In carrying out this invention, for every 100 parts of cellulose, is taken 350 parts of acetic anhydride, 5 parts of phenol-sulfonic acid, and five parts of sodium phenolsulfonate, or other salt of phenolsulfonic acid. The patentees' contention that the presence of the stated amount of sodium phenol-sulfonate "positively insures the absence of sulfuric acid during the operation" has been disproved by the experiments of Schwalbe.[2] For the dilution

1. U.S.P. 709922, 1902; abst. J.S.C.I. 1902, 21, 1345, E.P. 20660, 1902; abst. J.S.C.I. 1903, 22, 1011. F.P. 324862, 1902; abst. J.S.C.I. 1903, 22, 646; Mon. Sci. 1904, (4), 60, 43. Knoll & Co. (E.P. 8990, 1912; abst. C.A. 1913, 7, 3118; J.S.C.I. 1913, 32, 823) take cellulose acetates insoluble in chloroform and render them soluble by treatment with such catalysts as sulfuric acid, neutral salts; bisulfates such as methylamine bisulfate, or organic sulfonic or sulfinic acids.

2. l. c. He says: According to the patent specification, free sulfuric acid is said to have very injurious effect. Therefore, to exclude its presence as an impurity in the starting material or to prevent its formation during the process of acetylation, the example given in the specification directs the simultaneous use of phenol sulfonic acid and sodium sulfophenolate. The latter substance is added for the purpose of combining with free sulfuric acid, which is said not to be capable of existence in the presence of salt. Among the reacting materials used the acetic anhydride might contain sulfuric acid. Much greater might be the percentage of sulfuric acid in the technical phenolsulfonic acids. It is known how easily decomposable the technical phenolsulfonic acids are. In a recently published article Obermueller (Ber. 1907, 40, 3632) writes about these acids:

"I have been prevented from producing these acids in solid form, because they are ever so much more easily decomposed in a free state, and very difficult to produce in a pure form."

Indeed, in ordinary mixture of the barium salts of the two phenolsulfonic acids is prepared, and their solution decomposed with a little less than the calculated amount of sulfuric acid, solutions of free phenolsulfonic acid are obtained, which at once give off the odor of phenol when evaporated on the water bath and contain free sulfuric acid. It is therefore impossible in the usual way to obtain this acid as a dry or solid body, but one must be satisfied to produce it as a moist, deliquescent, crystalline mass. Now, it is

of the above acetylating mixture, about 350 gms. of glacial

claimed that the presence of sodium phenolsulfonate prevents the existence of free sulfuric acid in the acetylation with acetic anhydride. The question is whether this decomposition between free sulfuric acid and the sodium salt proceeds so rapidly that in the acetylation proper, cellulose is in contact with a liquid free from sulfuric acid. The experiment indicates that the decomposition proceeds extraordinarily slow for if a mixture of 35 parts acetic anhydride, 0.5 parts phenolsulfonic acid and 0.5 parts sodium phenolsulfonate are heated to 80°, according to directions taken from the patent specification, then after three to four hours, sulfuric acid can be plainly shown, and only after twelve to fifteen hours is the liquid free from the presence of uncombined sulfuric acid. The slow reaction is explained by the fact that sodium phenolsulfonate is difficultly soluble in acetic anhydride. The same is the case with the free sulfonic acid, while, as is well known, sulfuric acid is very easily soluble in acetic anhydride. Consequently during acetylization, the liquid contains free sulfuric acid. As is shown in Lederer's D.R.P. 163316, hydrocellulose is formed after one hour's heating with glacial acetic acid containing sulfuric acid. It therefore is highly probable that sulfuric acid, and not phenolsulfonic acid, causes acetylization.

But it is not at all impossible that pure phenolsulfonic acid might act as an esterifying agent, and the formation of hydrocelluloses and its esterification by sulfuric acid might only be a secondary reaction. This question might be settled by carrying out acetylation of cellulose with pure phenolsulfonic acid and acetic anhydride both free from sulfuric acid. Pure phenolsulfonic acid may be obtained if the liquid produced by conversion of the solution of barium phenolsulfonate with sulfuric acid is evaporated at 30-40° in vacuo, a faintly pink colored crystalline mass being obtained which is entirely free from sulfuric acid and does not possess the phenol odor. According to the directions of the patent specification, if cotton cellulose and pure phenolsulfonic acid or the sodium salt, and acetic anhydride are heated together for five to seven hours at 70-80°, cellulose is changed into a slimy, syrupy mass. By kneading the reaction mass with water, acetyl cellulose separates out, which is washed, dried and examined according to the method described in the experimental part of this publication. The cellulose thus separated from Mork's acetyl cellulose has a copper figure of 2.8. This figure is lower than that obtained with Lederer's and Bayer's products, but it must be borne in mind that the experiment was carried out with phenolsulfonic acid completely free from sulfuric acid, and therefore at the commencement much less sulfuric acid was present than when the directions of the patent specification are adhered to. At any rate, hydrolysis has taken place, which can only be due to the phenolsulfonic acid or to its decomposition products. If free phenolsulfonic acid is suspended in acetic anhydride and heated to 70-80°, a splitting off of sulfuric acid cannot be demonstrated, but this can be done in the presence of cotton cellulose. If an acetylization mixture prepared according to directions, employing, however, reagents free from sulfuric acid, is tested every hour by examining trial portions, then it is possible to determine the presence of sulfuric acid up to four hours. For these tests 3-4 cc. liquid were taken, diluted with water, heated to boiling, and to the boiling liquid barium chloride is added. Turbity is observed at once and after

acetic acid is added. The esterification is preferably carried on at about a temperature of 80°, with stirring in order to insure even acetylation.

To minimise the degrading action of the sulfuric acid on cellulose it has been proposed to add sodium acetate to the esterizing mixture [1] in order to induce double decomposition between sulfuric acid and sodium acetate, whereby the sodium combines with a portion, at least, of the free sulfuric acid. It is a fact that the addition of alkaline acetate materially decreases the danger caused by larger amounts of vigorous condensing agents such as sulfuric acid. This invention can be carried out by introducing into a solution of acetylcellulose prepared in the usual manner with sulfuric acid, acetic acid and anhydride, a quantity of dry, pulverized sodium acetate, in quantity about twice the amount of sulfuric acid used. The sodium acetate is introduced at that stage of the process when a diminution of viscosity shows the esterifying process to be nearly complete. If the solution is too viscous, the anhydrous sodium acetate may first be dissolved in a small amount of acetic acid before introduction, and then stirred in small portions at a time. In this manner it is claimed the solution can be filtered and directly spun into threads without precipitating, washing, drying, and dissolving as is usually done. Instead of sodium acetate, the corresponding quantity of ammonia, ammonium acetate, alkylated ammonias and their salts with weak acids may be used. In another method,[2] nitrates are claimed as eminently suited for this purpose, the liberated nitric acid exerting but little injur-

standing for several hours, a precipitate is formed. The splitting off of sulfuric acid is, therefore, proven.

1. E.P. 8727, 1908; abst. J.S.C.I. 1908, **27**, 996. Add. 9194, dated April 16, 1908, to F.P. 376578, 1907; abst. J.S.C.I. 1908, **27**, 996. D.R.P. 201910, 1907; abst. Chem. Zts. 1909, **8**, 1052; Zts. ang. Chem. 1908, **21**, 2333; Chem. Zentr. 1908, I, 1349; II, 1310; Mon. Sci. 1912, **76**, 57. D.R.P. 201910, being addition to D.R.P. 196730, 1906; abst. Mon. Sci. 1912, **77**, 57. Belg. P. 199492, 1907.

2. E.P. 8369, 1907; abst. J.S.C.I. 1907, **26**, 1213. F.P. 376578, 1907; abst. J.S.C.I. 1907, **26**, 988; Mon. Sci. 1908, (4), **68**, 88. D.R.P. 196730, 1906; abst. C.A. 1908, **2**, 2301; Mon. Sci. 1911, (5), **74**, 92; Chem. Zts. 1908, **7**, 806; Zts. ang. Chem. 1908, **21**, 1194; Jahr. Chem. 1905-08, II, 989; Chem. Ind. 1908, **31**, 422; Wagn. Jahr. 1908, II, 365. Aust. P. 36126, 37138.

ious influence either on the stability of the solutions, or on the elasticity of the acetated cellulose obtainable, but may improve the appearance of the latter owing to the bleaching action.[1] Finely pulverized ammonium nitrate has been found to so retard the action of sulfuric acid on the acetated cellulose, that the acetating mixture after filtration may be worked into threads, films and celluloid-like masses without washing or re-dissolving the acetylcellulose.

As far back as 1904, A. Corti and the Fabrique de Prod uits Chimiques Flora Societe Anonyme [2] found that cellulose could be acetylated by means of acetic acid and anhydride, useing dimethyl sulfate [3] in place of free sulfuric acid. By heating 30 parts of cotton or other form of cellulose with 70 parts of acetic anhydride, 120 parts of glacial acetic acid and 3 parts dimethyl sulfate until dissolution is almost complete, there is formed after precipitation in water and neutralization, an acetated cellulose soluble in acetic acid, chloroform, acetone, and insoluble in alcohol or ether. During the operation it is claimed the temperature may reach 130° (F. or C., not stated), and that either pure, freshly distilled, or commercial dimethyl sulfate may be used with advantage.[4]

1. L. Lederer (E.P. 26502, 1906; abst. J.S.C.I. 1907, **26**, 634. F.P. 371357, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 79. Belg. P. 195839, 1906) endeavors to overcome the injurious effect of the condensing medium so that the solution may be directly used for filament formation. To this end he adds such basic substances as methylamine, guanidine, aniline, amido-phenols and their esters and ethers, as well as alkaline salts of formic and acetic acids, as potassium acetate.

2. U.S.P. 826229, 1906; abst. J.S.C.I. 1906, **25**, 825; Mon. Sci. 1907, (4), **66**, 35; E.P. 9998, 1905; abst. J.S.C.I. 1905, **24**, 855. F.P. 345764, 1904; abst. J.S.C.I. 1905, **24**, 40; Mat. Color. 1905, **9**, 53; Mon. Sci. 1906, (4), **64**, 12. D.R. Appl. C.-12963, 1903. Belg. P. 183877, 1905. It. Appl. P. dated April 17, 1905.

3. Dimethyl sulfate is an oily liquid of sp. gr. 1.33 at 15° and boiling with partial decomposition at 188°. Diethyl sulfate (L. Lilienfeld, E.P. 13882, 1913; F.P. 459282, 1913; U.S.P. 1074633, 1913; abst. C.A. 1913, **7**, 4046; J.S.C.I. 1913, **32**, 1030, 1130) may be prepared by distilling sodium ethyl sulfate in a vacuum, with or without the addition of a suitable diluent. See L. Lilienfeld. E.P. 6387, 1913; abst. Kunst. 1914, **4**, 256.

4. An important question in patent litigation is brought out in this and similar patents in respect to the effect of sulfuric acid on the cellulose and the esterizing bath. It is a debatable question whether hydrocellulose is first formed from cellulose and then acetated, or whether cellulose is acetated, and then hydrolyzed, i. e.,

The sulfinic acids as benzol-sulfinic[1] in the hands of Knoll and Co.,[2] the ethyl-sulfuric acid[3] process of C. E. whether acetylation of hydrocellulose, or hydrolysis of acetated cellulose occurs. If the sulfuric acid, for instance, first hydrolyzes, and this hydrolyzed product is then acetated, it must follow that the condensing power of the sulfuric acid in this capacity is in the role of a catalytic.

1. One part of cotton or other form of cellulose is introduced into a mixture of 8 parts glacial acetic acid, 4-8 parts benzolsulfinic acid and 3 parts acetic anhydride, the ester going into solution at 50-60° in about 1.5 hours, and at lower temperatures requiring a correspondingly longer time. E. Knoevenagel has pointed out (U. S.P. 1090074, 1914; abst. C.A. 1914, **8**, 1667; J.S.C.I. 1914, **33**, 349) that the effect produced by sulfinic acids is similar to that obtained with sulfuric acid or aromatic sulfo-acids for the manufacture of cellulose acetates, although the sulfinic acids are considered derivatives of sulfurous acid. While the composition of the sulfinic acids is analogous to that of sulfurous acid, the two groups of acids differ essentially as regards their chemical and physical properties. The claimed advantages of the sulfinic over sulfuric and the aromatic sulfonic acids are that cellulose acetate solutions prepared with sulfinic acids may be kept for months without appreciably losing their viscosity, while solutions prepared with a comparatively large quantity of sulfinic acid may be boiled down in vacuo at temperatures up to 80° nearly to dryness without undergoing decomposition. In the preferred process of Knoevenagel, one part of cellulose (fibrous cotton) is introduced into a mixture of 5 parts of acetic anhydride, 4 parts of glacial acetic acid and 0.1-0.2 parts of benzene-sulfinic acid, and the mixture heated to about 50° for 10-24 hours. At the end of this time a clear viscid solution has been formed, from which the esterized cellulose may be precipitated by alcohol or water in the usual manner.

2. E.P. 2026, 1907; abst. J.S.C.I. 1907, **27**, 353. F.P. 369123, 1906; abst. J.S.C.I. 1907, **26**, 91; Mon. Sci. 1908, (4), **68**, 28. D.R.P. 180666, 1905; abst. Zts. ang. Chem. 1907, **20**, 1786; Mon. Sci. 1909, (4), **70**, 77; Jahr. Chem. 1905-08, II, 982; Wagn. Jahr. 1907, II, 404. D.R.P. 180667, 1905, being Addition to D.R.P. 180666, 1905; abst. Chem. Ind. 1907, **30**, 110; Zts. ang. Chem. 1907, **20**, 1786; Mon. Sci. 1909, (4), **70**, 77; Jahr. Chem. 1905-08, II, 982. Knoll & Co. (D.R.P. 272121, 1911; abst. J.S.C.I. 1914, **33**, 640; Kunst. 1914, **8**, 192), prefer as an ester, sulfuric acid, acid sodium ethyl-sulfate, a chloroform soluble and acetone insoluble ester resulting when one part of cellulose is acted upon at 100° with four parts each acetic anhydride and glacial acetic acid and 0.04 part acid sodium ethyl sulfate.

3. C. E. Dreyfus claims to be able to produce cellulose esters even in cold by the action of formic acid or the acid chlorides or anhydrides of aliphatic acids on cellulose or its derivatives in the presence of a small quantity of an aliphatic or aromatic ester of sulfuric acid. If the reaction is carried out in the absence of solvents, gelatinous products are obtained; if in the presence of a solvent such as acetic acid or chloroform, viscous solutions are produced which can be directly spun. Example: 10 kilos of cellulose are mixed with 30 kilos. of acetic anhydride, 30 kilos. of glacial acetic acid and 200 grms. of ethylsulfuric acid, and the mixture well stirred at the ordinary temperature until complete solution is obtained.

Dreyfus,[1] or the aniline bisulfate[2] method of F. Bayer & Co.,[3] are but extensions of the principal of endeavoring to modify, temper, or reduce the destructive condensing action of sulfuric acid in the esterification of cellulose.

In a quite recent process,[4] alkylamine sulfuric salts and

The cellulose ester is then precipitated by pouring the solution into water.

1. F.P. 430606, 1911; abst. J.S.C.I. 1911, **30**, 1375.

2. The process consists in treating cellulose, either normal or modified, with acetylizing agents and acid sulfates (primary sulfates) of primary aromatic amines, as aniline bisulfate. For example—treat 20 parts of cellulose with a mixture of 8 parts *o*-toluidine bisulfate, 120 parts glacial acetic acid and 100 parts acetic anhydride, at a temperature of about 30°, most of the bisulfate going into solution. The cellulose slowly softens and is dissolved after some hours. It is then further stirred at a temperature lower than 70° until it is soluble in acetone, then precipitated and further treated in the usual manner. It is a whitish, granular powder, soluble in acetone, a mixture of ethyl acetate and alcohol (4:1), a mixture of chloroform and alcohol or nitrobenzene and alcohol. Knoll & Co. (E.P. 8990, 1912. F.P. 453835; E.P. 2491, 1913; abst. Kunst. 1913, **3**, 415, 416; C.A. 1914, **8**, 248; J.S.C.I. 1913, **32**, 785; 1914, **33**, 308) acetylate cellulose with 4 parts acetic anhydride, 5 parts glacial acetic acid, and 0.1 part methylamine bisulfate at a temperature of about 70°. 0.025 parts sulfoacetic acid, or 0.015 parts sulfuric acid may be added.

3. U.S.P. 987692, 1911; abst. J.S.C.I. 1911, **30**, 485; Chem. Tech. Rep. 1911, **35**, 250. E.P. 14271, 1910; abst. J.S.C.I. 1911, **30**, 485. F.P. 417274, 1910; abst. J.S.C.I. 1911, **30**, 485. See also A. Eichengruen and F. Bayer & Co., Aust. Anm. 27258, 1910; 237, 1910; 5012, 1910; 5896, 1910; Aust. P. 52289, 1911; 50331, 1912. Hung. Anm. E.-1568, Jan. 13, 1910. Swiss P. 52273, 1910; 53888, 1910, being Addition to 52273; 57952, 1910. Belg. P. 226582, 1910; 227385, 1910. D.R. Anm. F.-32823. D.R.P. 233786, 1911. D.R. Anm. E.-1558, Dec. 27, 1909, being Addition to F.-14998; abst. Kunst. 1912, **2**, 340, 359. In Add. 18345, to F.P. 417274, 1910; abst. Kunst. 1914, **4**, 235; J.S.C.I. 1914, **33**, 478, acid sulfates of aromatic amines may be replaced by neutral sulfates of amines. Example: 50 parts of cellulose are acetylated by a mixture of 250 parts of acetic anhydride, 200 of glacial acetic acid and 20 of methylamine sulfate or *o*-toluidine sulfate, at 30-60°. The product obtained is soluble in a mixture of ethyl acetate and ethyl alcohol 4:1, in a mixture of chloroform and alcohol, and of nitrobenzene and alcohol. Aniline sulfate is also claimed as efficient.

4. A. Loose and Chem. Fabr. auf. Aktien (vorm. E. Schering), U.S.P. 1069445, 1913; abst. J.S.C.I. 1913, **32**, 865; Mon. Sci. 1914, **80**, 39; Chem. Abst. 1913, **7**, 3227. E.P. 27227, 1912; abst. J.S.C.I. 1913, **32**, 696; Kunst. 1913, **3**, 395; C.A. 1913, **7**, 4069. E.P. 27228, 1912; abst. J.S.C.I. 1913, **32**, 530; C.A. 1914, **8**, 1668. E.P. 2178, 1913; abst. Kunst. 1914, **4**, 15; J.S.C.I. 1913, **32**, 975. F.P. 450890, 1912; abst. J.S.C.I. 1913, **32**, 531; Kunst. 1913, **3**, 195; C.A. 1913, **7**, 3227; Mon. Sci. 1914, **80**, 6. F.P. 452374, 1912; abst. Kunst. 1913, **3**, 274; Mon. Sci. 1914, **80**, 8; J.S.C.I. 1913, **32**, 652; C.A. 1913, **7**, 3663. Belg. P. 251010; abst. Kunst. 1913, **3**, 235. Belg.

esters are employed as catalytic agents in the acetylation of cellulose or its more immediate transformation products, the sulfates of hydrazine or hydroxylamine being claimed as especially suitable. To carry this invention into effect, 20 parts of cellulose are first impregnated with a solution of 2 parts of hydrazine sulfate, dried and acetylated with a mixture of 100 parts glacial acetic acid and 100 parts of acetic anhydride. Or, 0.5 part of finely powdered hydroxylamine sulfate is suspended in a mixture of 100 parts each of glacial acetic acid and acetic anhydride, 20 parts of cellulose being then introduced. In both cases reaction starts at the ordinary temperature and is completed within 2 to 6 hours.

Anhydrous copper salts form the novelty of the process of F. Paschke and the Safety Celluloid Co.,[1] the cellulose acetate being manufactured by the action upon cellulose of a mixture of acetic anhydride and glacial acetic acid in conjunction with a suitable anhydrous copper salt, e. g., the sulfate, nitrate, chloride or a mixture of the acetate and nitrate. The product is subjected to a partial de-acetylation by the action of chlorine. Example: 200 kilos of cellulose are treated at a temperature of 70° with 1300 kilos. of a mixture of 30 per cent. of acetic anhydride and 70 per cent. of glacial acetic acid, in which 5 kilos of anhydrous copper sulfate are dissolved. After the reaction, 600 kilos. of 80 per cent. acetic acid are added and the product poured into jars in which it is treated with chlorine in the proportion of about 2 parts of chlorine per 100 of cellulose at a temperature which must not exeed 60°. De-acetylation is thereby produced and should be stopped when the product contains 50-55 per cent. of combined acetic acid. This state is reached when the product is soluble in ethyl acetate, and may be recognized by a fall in

P. 251011; abst. Kunst. 1913, **8**, 235. Belg. P. 252882; abst. Kunst. 1913, **8**, 275. D.R. Anm. 12o, C.-21388, dated Dec. 18, 1911; abst. Kunst. 1913, **8**, 20. See their D.R. Anm. C.-21994 and C.-23703; Add. 17104 to F.P. 452374; abst. Kunst. 1913, **8**, 416; C.A. 1913, **7**, 4069; J.S.C.I. 1913, **32**, 784. Also their E.P. 2178, 1913; abst. C.A. 1914, **8**, 2620.

1. E.P. 15868, 1912; abst. J.S.C.I. 1913, **32**, 192; C.A. 1913, **7**, 3025. U.S.P. 1082167, 1913; abst. J.S.C.I. 1914, **33**, 72; C.A. 1914, **8**, 821. F.P. 458263, 1913; abst. J.S.C.I. 1913, **32**, 1064. Badische Anilin und Soda Fabrik, E.P. 14042, 1914.

the specific rotatory power from $[a]_D = -21°$ to $[a]_D = -7°$. At that stage water is added to precipitate the ester as a flocculent mass.

In another process[1] it is recommended to subject the cellulose to the action of nitric and sulfuric acid containing much water, a cellulose being obtained which is completely converted and contains a small amount of nitrogen, but does not possess the characteristic properties of typical nitrocellulose. If a fatty acid anhydride as acetic anhydride be now allowed to act upon this product in the presence of a suitable catalyzer, cellulose esters result which are said to be especially applicable for the manufacture of photographic films.

In the manufacture of cellulose esters in the presence of (so-called) neutral salts, Knoll & Co.[2] recommend the use of ferrous sulfate, ferric chloride or sulfate, zinc sulfate or chloride, cupric sulfate, stannous chloride, antimony trichloride, ammonium sulfate, the chlorides of ammonium, magnesium or calcium, dimethylamine chloride or diethylamine sulfate. Examples characteristic of the working of the process are given in the original patents.[3]

1. E.P. 10706, 1912; abst. C.A. 1913, **7**, 3414. Compare E.P. 1156, 1914, Add. to E.P. 10706, 1912; abst. J.S.C.I. 1914, **8**, 688.

2. D.R.P. 203178, 1906; abst. Jahr. Chem. 1905-08, 984; Chem. Zentr. 1908, **79**, (5), **12**, 1549; Chem. Zts. 1909, **8**, 1053; Mon. Sci. 1912, **77**, 96; Zts. ang. Chem. 1908, **21**, 2426; Wagn. Jahr. 1908, **54**, 366. D.R.P. 206950, 1907, being Addition to D.R.P. 203178, 1906; abst. Chem. Zts. 1909, **8**, 1183; Zts. ang. Chem. 1909, **22**, 656; Mon. Sci. 1912, **77**, 96; Chem. Ind. 1909, **32**, 153; Wagn. Jahr. 1909, **55**, II, 397; Jahr. Chem. 1909, 386. E.P. 2026A, 1907; abst. J.S.C.I. 1908, **27**, 353.

3. Example 1: To a mixture of 5 parts of acetic anhydride and 4 parts of glacial acetic acid are added 0.1 to 0.2 parts of finely pulverized iron vitriol and one part of cellulose (for instance cotton). The whole is thoroughly mixed and placed in a bath at about 70°. Solution of the cellulose in the form of acetates takes place in about 15 to 24 hours, the result being a thick liquid.

Example 2: To a mixture of 5 parts of acetic anhydride and 4 parts of glacial acetic acid are added 0.1-0.2 parts of finely pulverized ferric chloride containing water of crystallization, and one part of cellulose. In a bath of about 50° solution in the form of cellulose acetate takes place in 8-12 hours.

Example 3: To a mixture of 5 parts of acetic anhydride and 4 parts of glacial acetic acid are added 0.2 parts of zinc chloride and one part of cellulose, such as cotton wool, which may have a per-

C. Claessen [1] prepares esters of hydrolyzed cellulose which are soluble in water, dilute alcohol, dilute acetone and glycerol, but insoluble in pure alcohol, anhydrous acetone, ether or benzene, by treatment of cellulose with a fatty acid anhydride at temperatures of 70°-80°, in the presence of acid sulfates of pyridine or its homologues or quinoline sulfate. Where the esterification is carried out in the presence of a suitable solvent as glacial acetic acid, the ester is obtained in the form of a clear viscous solution, from which it may be precipitated by means of alkalis, ammonia or water.

According to E. Knoevenagel [2] viscous solutions of acetyl cellulose can be made by dissolving cellulose 10 in a mixture of glacial acetic acid 40, benzene sulfinic acid 1-2 and acetic anhydride 50 parts by heating to 50° for 10-24 hours. It is claimed that the solution may be boiled *in vacuo* to almost complete dryness at temperatures up to 80° without decomposing, and may be used for making artificial silk and films.

Manufacture of Cellulose Acetate with Zinc Chloride. Franchimont, in 1879, was the one to first describe the use of fused zinc chloride in the acetation of cellulose and other carbohydrates. Zinc chloride has the advantage over sulfuric acid as a catalytic agent in acetation, in that a more elevated temperature of esterification can be maintained with less injury to the cellulose acetate formed, while the subsequent partial hydration may be carried on at considerably higher temperatures without danger of breaking down, and hence proneness to the formation of weak films. As compared with sulfuric acid, cost of acetation is greater; usually requires a longer time for the completion of the process; there is less

centage of moisture much in excess of the normal (6%). In a bath of about 70° dissolution takes place in 12-24 hours whereby very clear and highly viscous solutions of cellulose acetates are obtained.

Example 4: One part of cotton is added to a solution of 0.25 parts of hydro-chlorate of dimethylamine in 5 parts of acetic anhydride and 4 parts of glacial acetic acid, and the whole heated to about 70°. After 80-100 hours a uniform viscous solution of cellulose acetate is obtained.

1. D.R.P. 222450, 1908; abst. J.S.C.I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Wagn. Jahr. 1910, **56**, II, 434; Chem. Zentr. 1910, **81**, 48; Chem. Zts. 1910, **9**, 1902; C.A. 1910, **4**, 2875.

2. F.P. 369123, 1906; U.S.P. 1090074, 1914; abst. C.A. 1914, **8**, 1667; J.S.C.I. 1907, **26**, 91; 1914, **33**, 349.

degradation of the cellulose and cellulose acetate; and the process of hydration can be modified, checked or otherwise kept under control more readily than where the more energetic mineral acid is used. In partial hydration, a great deal more water is necessary to obtain a determined solubility than where sulfuric acid is employed.

The following is a practical process of acetation and subsequent partial hydration with zinc chloride as the sole catalyzer. Dissolve 10 gms. zinc chloride (preferably fused) in 100 cc. glacial acetic acid of at least 99.5% strength, using a gentle heat to facilitate the solution of the zinc chloride in the acid, the result being a clear syrupy liquid. To this add 100 cc. glacial acetic acid and 150 cc. acetic anhydride of at least 90% strength in anhydride, mix, and place therein 50 gms. of oven dried, bleached, absorbent cotton, keeping the temperature of the acetation both around 60° in order to facilitate solution of the cotton. The mass is stirred, and the temperature kept about 60°, until all the cotton has passed into solution in the reacting mixture, forming a heavy, viscous and practically colorless fluid. In about three hours after the introduction of the cotton, and depending somewhat upon the length of time and vigor with which the solution has been stirred and the temperature maintained, the solution, which should be nearly clear and have at the most but a few unacted upon filaments in suspension, is ready for partial hydration.

The amount of water required for hydration will depend primarily upon how much acetic anhydride has been vaporized during the stirring of the acetation period. In general, a mixture of 70 cc. water to which is added 50-70 cc. glacial acetic acid to minimize precipitation of the acetated cellulose upon introduction of water into the acetating bath, will be found sufficient, the temperature of partial hydration being kept at 60°-65°, with occasional stirring, until a test portion withdrawn gives the solubility determinations required. For film formation, and the production of filaments, films and bands of maximum strength, tenuity and flexibility, the point at which hydration should be interrupted, is when a test portion precipitated in water, washed to neutrality and dried, is found

completely soluble in anhydrous, absolute acetone, and plastic, but not dissolving, in warm alcohol-free chloroform. When the hydration has reached this stage, the plasticity in warm chloroform, will change to an entire solubility, if a few drops of alcohol are added to the chloroformic solution. The acetated mass, still a clear, viscous solution, is then stirred into a large bulk of cold water, rapidly broken up that hydration may not continue, washed to neutrality and dried at a low temperature. Acetated cellulose precipitated from solutions in which zinc chloride is used as the catalyzer, is usually obtained as a tough fibrous white, amorphous and stringy mass, especially where the hydration has been stopped at a solubility in absolute acetone. If the water used for hydration be replaced by an equal volume of hydrogen dioxide solution, the resulting acetate precipitates out in a snow white condition. Where the acetated cellulose passes into solution in the reacting mixture, zinc chloride is probably the safest practical catalyzer to use, especially when operating on large quantities of cellulose, where reduction of temperature quickly during acetation is difficult without the use of artificial refrigeration. The author has examined samples of Cellit, a commercial partially hydrolyzed acetated cellulose, from which the fibrous character of the product, and the presence of small amounts of salts in the ash, would indicate zinc chloride or similarly acting salt had been employed as catalyzer. Whereas with sulfuric acid as catalyzer it is policy to stir the cellulose until practically disintegrated before the temperature is allowed to rise, with zinc chloride this precaution is unnecessary in order to insure uniform acetation.

Acetation with Substituted Acetic Acids. Both monochlor-, dichlor-, and trichlor-acetic acids have been patented as condensing agents in the formation of cellulose esters. In one process,[1] 1 part of cellulose, 5 parts acetic anhydride and 4

1. Knoll & Co., D.R.P. 203642, 1906; abst. Zts. ang. Chem. 1908, **21**, 2334, 2426; Chem. Zts. 1909, **8**, 1218; Wagn. Jahr. 1908, II, 367; Chem. Zentr. 1908, II, 1705; Jahr. Chem. 1905-08, II, 983; Chem. Ind. 1908, **31**, 711; Mon. Sci. 1912, **77**, 96. Belg. P. 199492, 1907. For manufacture of dichloracetic acid, see K. Brand, D.R.P. 246661, 1911; abst. J.S.C.I. 1912, **31**, 796; Chem. Zentr. 1912, I, 1742; Zts. ang. Chem. 1912, **25**, 1657; Wagn. Jahr. 1912, II, 40.

parts glacial acetic acid are heated to about 70° for 200-300 hours with 0.2-0.3 parts of monochloracetic acid, after which time the cellulose has acetylated and formed a thick liquid. Or, 1 part of cellulose, 2 parts glacial acetic acid and 2 parts trichloracetic acid are heated for 90 hours to 70°. A very thick and viscous solution results. In another process [1] 3 parts cellulose is heated on the water bath at 50°-55° with 8 parts monochloracetic acid and 16 parts acetic anhydride. After standing, a heavy, viscous solution results, which upon further standing becomes clear, and is then ready for precipitation, washing and drying.

Another method depends upon the use of sulfacetic acid for its claim to originality, 5 parts of sulfacetic acid being added to 100 parts of a mixture of equal quantities of acetic anhydride and glacial acetic acid. The sulfacetic acid is obtained by dissolving 10 gms. of sulfuric acid 66° Be. strength, in 30 gms. acetic anhydride and heating to a temperature not exceeding 130°. To 10 parts of acetylating mixture thus prepared is added 1 part of cellulose or hydrocellulose, and the whole mass heated to 50°-70° until a clear solution is obtained. The acetylated cellulose is then separated from the solution in any convenient manner.[2]

Acetation in Presence of Chlorides. In the acetylization of normal cellulose direct, instead of first converting it as a distinct process into hydrocellulose or oxycellulose, the mineral acid usually employed may be replaced by the anhydrochloride of a mineral acid, the conversion of the cellulose into soluble acetylized derivatives being complete, or practically so. Suitable mineral acid anhydrochlorides are phosphorous pentachloride and oxychloride [3] and the chlorides and oxy-

1. Actien-Gesellschaft fur Anilin-Fabrikation, E.P. 14255, 1906; abst. J.S.C.I. 1907, **26**, 220; C.A. 1907, **1**, 1341. F.P. 368738, 1906; abst. J.S.C.I. 1907, **26**, 30. D.R.P. 198482, 1905; abst. Mon. Sci. 1911, (5), **74**, 54; Zts. ang. Chem. 1908, **21**, 1760; Chem. Zentr. 1908, II, 118; Jahr. Chem. 1905-08, II, 982; Chem. Ind. 1908, **31**, 378; Wagn. Jahr. 1900, II, 362.

2. Societe Anonyme D'Explosifs et de produits Chimiques, F.P. 385179, 1907; Mon. Sci. 1909, (4), **70**, 105; Bull. Soc. Chim. 1909, (4), **6**, 557; J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383. F.P. 385180, 1907; Mon. Sci. 1909, (4), **70**, 106; Bull. Soc. Chim. 1909, (4), **6**, 557; J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383.

3. E.P. 10243, 1903; abst. J.S.C.I. 1904, **23**, 557.

chlorides of sulfuric acid.[1] Of the chlorides of phosphorus, the oxychloride in practice has been found preferable. They combine with water with great avidity with production of the corresponding hydrated mineral acid and gaseous hydrochloric acid, and although where, for example, phosphorous oxychloride and acetic anhydride are used, there is produced in the course of the reaction, phosphoric acid and hydrochloric acid, the results obtained are claimed as distinctly superior to those resulting from the employment of the hydrated acids direct. The proportion of anhydrochloride necessary may vary within wide limits according to the particular anhydrochloride selected.[2]

Of the sulfuric acid chlorides, it has been claimed that SO_2OHCl, SO_2Cl_2 and $S_2O_5Cl_2$ are superior to the chlorides of phosphorus. It is a fact that whilst sulfuric acid at or above 50°, except in very small quantities, destroys the solution of acetylized cellulose *in statu nascendi*, by decomposing it and rendering it dark, sulfuryl chloride under the same conditions of heat and length of time of action upon the acetylated cellulose, produces solutions of much lighter color, and considerably greater viscosity and clearness.[3]

1. E.P. 24382, 1910; abst. J.S.C.I. 1911, **30**, 616; C.A. 1911, **5**, 3157. F.P. 423197, 1910; abst. J.S.C.I. 1911, **30**, 615; Chem. Tech. Rep. 1911, **35**, 307. Swiss P. 54497, 1910. Belg. P. 229995, 1910. U.S.P. 1051165, 1913; abst. J.S.C.I. 1913, **32**, 192; Kunst. 1913, **3**, 275; Mon. Sci. 1913, **79**, 107. D.R.P. 269193, 1909; abst. Kunst. 1914, **4**, 20, 97; C.A. 1914, **8**, 2251. Aust P. 12 e A. 8062, 1910; abst. Kunst. 1912, **2**, 460. In a later process (D.R.P. 273029, 1910; Add. to D.R.P. 269193; abst. Kunst. 1914, **4**, 234) improvements due to the use of pyrosulfuryl chloride are described by Chem. Fabrik von Heyden.

2. According to E.P. 10243, 1902, 10 parts by weight of dry fibrous cellulose in the form of purified cotton are steeped in a mixture of 30 parts by weight of acetic anhydride and 30 parts by weight of glacial acetic acid, contained in a stoppered bottle and to which have been added about 1.7 parts by weight of phosphorous oxychloride ($POCl_3$). The bottle is placed for about 7 or 8 hours in a chamber that is heated to and maintained at a temperature of 55°. The mixture may be stirred occasionally during the reaction. When the required solubility in chloroform or phenol has been attained, and this may vary according to the purpose for which the product is to be used, as found by testing from time to time, the termination of the reaction is brought about by adding water to the mixture under treatment.

3. E.P. 24382, 1910. Example 1: Ten parts by weight of cellulose in the form of cotton, wood cellulose, or other cellulose prod-

Knoll & Co.[1] have described the use of volatile mono-basic acids such as hydrochloric and nitric, ascribing advantages to the volatility of the acid employed, which appears not to enter into chemical combination in the acidylizing process, and also to their monobasicity, which causes any quantities of the acids which may combine with the cellulose to substantially lose their acid properties, which is not the case with polybasic non-volatile acids. The volatile acids are employed in the proportion of 0.1-0.3 parts by weight calculated on the weight of the cellulose, the acidylation being carried out at temperatures between 40° and 80°.[2] [3]

ucts, are heated to 50-80°, together with 18-20 parts of acetic anhydride, about 40-80 parts glacial acetic acid and one part sulfuryl chloride, until complete solution is effected. It is also possible to work with sulfuryl chloride without heating, if its quantity is increased. The solution takes place in some days (4-8) without substantial raising of the temperature. The sulfuryl chloride may be substituted wholly or in part by the above named other chlorides of sulfuric acid, e. g., pyrosulfuryl chloride and chlorosulfonic acid.

Example 2: Ten parts by weight of cellulose are soaked with 25 parts of acetic anhydride, 40-80 parts glacial acetic acid and one part pyrosulfuryl chloride. If the temperature is kept below 30° solution (acetylation) is complete in 24-48 hours.

Example 3: Ten parts by weight of cellulose are soaked with 50 or more of formic acid of 98-100% strength and 2-3 of sulfuryl chloride. Solution is complete in 1-5 days. It has been found advantageous not to employ cellulose free from all moisture, by drying it rapidly by artificial means, for instance at a temperature of about 105°.

1. U.S.P. 891218, 1908; abst. J.S.C.I. 1908, **27**, 765; Mon. Sci. 1909, (4), **70**, 116. E.P. 2026-B, 1907; abst. J.S.C.I. 1908, **27**, 353. F.P. 373994, 1907; abst. J.S.C.I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 83; Chem. Tech. Rep. 1907, **31**, 302. D.R.P. 201233, 1906; Chem. Zts. 1908, **7**, 993; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, 994; Chem. Ind. 1908, **31**, 587; Wagn. Jahr. 1908, II, 366; Jahr. Chem. 1905-08, 982. D.R.P. 203178, 1906; abst. Chem. Zts. 1909, **8**, 1053; Zts. ang. Chem. 1908, **21**, 2426; Chem. Zentr. 1908, **79**, 1837; Jahr. Chem. 1905-08, 984; Chem. Ind. 1908, **31**, 741. See also D.R. Anm. K.-50334, of Feb. 1, 1912, being addition to D.R.P. 203178, 1906; abst. Kunst. 1914, **4**, 160. Knoll & Co., D.R. Anm. K.-50960, K.-50605; both being addition to D.R.P Anm. K.-50333; abst. Kunst. 1914, **4**, 40, 179. In their D.R.P. 273029, 1910, Add. to D.R.P. 269193; abst. C.A. 1914, **8**, 2251, 2806, for the manufacture of fatty acid esters of cellulose or their closely related conversion products by means of fatty acid anhydrides in the presence of sulfur chlorides, in order to prevent great rise in temperature during the acetylation, the cotton is previously dried.

2. If attempts be made to acidylize with substantially smaller quantities than 0.1 parts of the acid to one part of cellulose (similar to the examples in the French patent 319648, e. g., with HCl in place of H_2SO_4) no acidylization at all takes place at ordinary tem-

Acetation Without Apparent Change in Structural Form. Unlike the cellulose nitrates which have many uses in the dry form, the literature or experience has not disclosed a single use to which the cellulose acetates in the dry or un-dissolved form have been used, or proposed for use.

In the presence of sulfuric acid the action of acetic acid and anhydride on cellulose, especially that regenerated from viscose and ammoniacal copper oxide, is very energetic, considerable heat is developed, and if the reaction is allowed to proceed unchecked the yield is much reduced, the cellulose degrading to the sugars—diglycose having been described as a sugar obtained in this manner. Furthermore many of the processes are open to the objection that the acetate is dissolved in the acetic acid or acetic anhydride used, and must be subsequently precipitated to be recovered. Often a portion only is recoverable after the cellulose acetate has passed into solution in the reacting mixture, so the yield is uncertain and for this reason unsatisfactory. If the reaction is carried out in the presence of a sufficient quantity of some non-reacting fluid and one in which cellulose acetate is insoluble (ether, benzine, benzene, toluene, carbon tetrachloride, etc.) the crude product does not lose the structural form of the original cellulose (if cotton), and separates in a crude state which may be directly purified.

peratures, even after a comparatively long time. If, under otherwise equal conditions, viz., while using less than 0.1 of the acid to one part of the cellulose, the reaction temperature be raised to 70°, for example, only complete acidylation takes place, even after a somewhat protracted period of time. The use of HCl in acetylization has also become known in another form by the research of Zd. H. Skraup and his collaborators (Wiener Monatshefte f. Chemie. 1905, 26, 1450). Whereas, however, the above investigators obtained at ordinary temperature by the action of acetic anhydride saturated with HCl gas, chloracetyl derivatives of cellulose and on prolonged action even secondary products thereof, the patentee, on the contrary, obtained pure acidyl derivatives, owing to the use of substantially smaller quantities of acid.

3. Example 1: Into a mixture of 5 parts of acetic anhydride and 4 parts of glacial acetic acid are led 0.1-0.2 parts of HCl gas, and after this one part of cellulose, e. g., wadding, is added. Solution as acetylcellulose takes place at about 70° within 30-40 hours.

Example 2: To 5 parts of propionic anhydride and 4-5 parts glacial acetic acid is added as much concentrated aqueous HCl as corresponds to 0.1 parts of hydrogen chloride. After the addition of one part of cellulose, solution as cellulose propionate takes place

L. Lederer first hydrolyzes cellulose[1] with an equal weight of glacial acetic acid containing 2.5% sulfuric acid, then three times the weight of carbon tetrachloride is added and the cellulose acetylated with 3.5 times the weight of acetic anhydride which has previously been diluted with an equal weight of carbon tetrachloride. At ordinary temperature the hydrolysis requires from 12-24 hours, the period of acetylation being less, and decreasing with rise in temperature of esterizing bath. At the completion of the operation the cellulose acetate, which has preserved the structure of the starting material, is separated from the fluid mass by pressure or centrifugalization, and freed from acid in the usual manner by washing and neutralization.

In the process of H. Mork[2] the cellulose is first converted into a "more reactive but still fibrous modification" by means of such hydrolyzing agents as hydrochloric or sulfuric acids. The invention may be carried out in practice as follows: A mixture is made of 400 parts of glacial acetic acid and 20 parts benzolsulfonic acid, into which is placed 100 gms. of high grade, bleached, cotton rovings. This is allowed to remain until thoroughly and uniformly saturated, when the cotton is pressed until it retains approximately one-half of the liquid originally employed. After standing for about 12 hours at 15°-20°, it will be found to have been converted into a highly reactive modification or form of cellulose in which the original structure is still present. The moist cellulose is next immersed in a bath of 300 parts acetic anhydride and 1200 parts benzol, and after immersion at room temperature for about 18 hours, and until a test sample removed has the desired solubility, it is centrifuged, washed and dried. The process patented in France by Societe Debauge et Cie.[3] is similar, benzene, at about 70° in 12-24 hours.

1. U.S.P. 999236, 1911; abst. J.S.C.I. 1911, **30**, 1050. E.P. 3103, 1907; abst. J.S.C.I. 1907, **26**, 889. F.P. 374370, 1907; abst. J.S.C.I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 84; Chem. Zts. 1907, **6**, 139. In this connection see D.R.P. 185151. F.P. 371356. Aust. P. 31203. See also Lederer, Belg. P. 244470, 1912; abst. Kunst. 1912, **2**, 399. E.P. 7687, 1912; abst. Kunst. 1913, **3**, 274.

2. U.S.P. 854374, 1907; abst. J.S.C.I. 1907, **26**, 713; Mon. Sci. 1907, (4), **66**, 159; C.A. 1907, **1**, 2316.

3. F.P. 450886, 1913; abst. Kunst. 1913, **3**, 195.

toluene, xylene or carbon tetrachloride being the inhibiting and diluting media in which the reaction is carried on.

The fact that the original structural form of the cellulose is conserved is of no apparent technical advantage, only the control resulting from the moderation induced by the dilution of the acetylizing liquid by these inert fluids, the ability to quickly lower the temperature by the introduction of cooled non-reacting liquids, and the influence of the benzene or its equivalent in restraining the reaction. The progress of the reaction can also be easily tested, and readily stopped by the addition of more diluent. Large quantities of cellulose may be esterified by these methods with a decreased danger of over acetylation, while the ease of removal of acid by washing, and the drying of the product in bulk are points of manufacturing interest.

The Societe Chimique des Usines du Rhone[1] propose to economize upon acetic anhydride—the most expensive constituent of the acetylating bath—by employing the vapors of acetic anhydride at boiling temperature. The two points of advantage claimed for this process is that the acetycellulose obtained retains the structure of the starting product, and the surplus anhydride and acetic acid may be afterwards recovered. The intensity of reaction may be moderated by reducing the pressure, lowering the temperature, or diluting the vapors. The process is carried out by placing in a cylindrical vessel whose top is connected to a condenser with vacuum pump, cotton impregnated with sulfuric acid as in the Girard hydrolyzing process, the pressure is reduced to 40 mm. and the cotton heated to 55°. The vessel is then connected to a steam heated boiler containing acetic anhydride, the latter being maintained at a temperature of 50-55°, and their pressure reduced until active ebullition commences. The anhydride

1. U.S.P. 1030311, 1912; J.S.C.I. 1912, **31**, 680; Mon. Sci. 1913, **78**, 14; C.A. 1912, **6**, 2528; Chem. Ztg. 1912, 485; Can. P. 139046, 1912; abst. C.A. 1912, **6**, 1526; E.P. 25893, 1912; abst. J.S.C.I. 1912, **31**, 279; Kunst. 1913, **3**, 174; C.A. 1913, **7**, 609. F.P. 437240, 1911; abst. J.S.C.I. 1912, **31**, 429; Mon. Sci. 1913, **78**, 134. D.R.P. 258879, 1910; abst. C.A. 1913, **7**, 3227; Kunst. 1913, **3**, 140. See also their E.P. 13696, 1914, for the manufacture of acid esters of cellulose.

vapors in their passage through the cotton rapidly esterify it, the issuing vapors being condensed. The reaction is terminated when a sample withdrawn is found soluble in chloroform. The anhydride vapors are then exhausted from the vessel, and the acetylated product washed and dried in the usual manner. It is claimed that the acetylcellulose so produced has the appearance and strength of the cotton employed ,and is soluble in chloroform, acetone, tetrachlorethane and glacial acetic acid.

There has been issued to H. Dreyfus a series of patents [1] in which is embodied a review of the majority of the points of merit in the acetylation of cellulose and its transformation products, some of the patents comprising as high as ten sheets of descriptive matter.

Knoll and Co.[2] describe the manufacture of cellulose acetate insoluble in acetic acid and chloroform. In their process, acetycellulose soluble in acetic acid and chloroform are left in contact with suitable catalysers, under such conditions that hydrolysis by water is avoided, until they become insoluble. Other substances may be added to the acetycellulose before the treatment. For example, a solution of acetylcellulose in glacial acetic acid is treated with sulfuric acid, sulfo-acetic acid, zinc chloride, or the like, until a solid product, insoluble in chloroform and acetic acid, is produced. Or, solid acetylcellulose, in a suitably subdivided form, may be left in contact with benzene, a little sulfo-acetic acid and a solvent for the latter, such as acetic anhydride or acid. The new acetycelluloses are soluble in formic acid, hydroxy-acids and their esters (e. g., tartaric acid esters), acid derivatives of hydroxy-acids and

1. F.P. 432046, 1911; First Add. 14558, dated July 7, 1911; Second Add. 14559, dated July 15, 1911; Third Add. 15933, dated Jan. 4, 1912; Fourth Add. 15894, dated April 1, 1912; Fifth Add. 16316, dated April 1, 1912; Sixth Add. dated Aug. 5, 1912; Seventh Add. 16494, dated Sept. 16, 1912; abst. J.S.C.I. 1912, **31**, 24, 225, 1119; 1913, **32**, 283, 420; Chem. Ztg. 1912, **34**, 1174. E.P. 20977, 20978, 20979, 1911; 20852, 21376, 22645, 1912. Belg. P. 241250, 246250, 246251, 1912; abst. Jour. Soc. Dyers, 1913, **29**, 91; J.S.C.I. 1913, **32**, 133, 1063; J.S.C.I. 1913, **32**, 891; Kunst. 1913, **3**, 95, 194, 434, 435. Belg. P. 241250, 246250, 246251, 1912. Port. 8348, 1912. Aust. P. 12-o, Mar. 16, 1910; Mar. 9, 1911. See also E.P. 19330, 1905; 26657, 1909; F.P. Add. 15933 to F.P. 432046; abst. Kunst. 1913, **3**, 435. D.R. Anm. D.-29439, 1913; abst. Kunst. 1913, **3**, 439.

2. D.R.P. 273706, 1911; abst. J.S.C.I. 1914, **33**, 746.

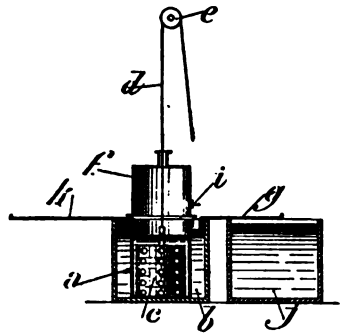
their esters (e. g., diacetyltartaric acid esters), acid derivatives of glycerol (acetins and chlorhydrins), nitromethane, and acetylene tetrachloride. They can be used for the preparation of artificial threads, films, celluloid, etc.

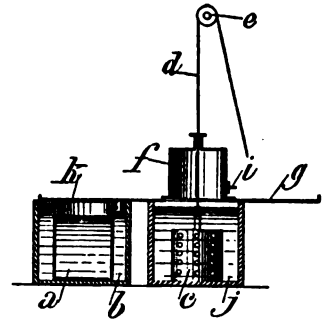
To still further decrease the inflammability of acetycellulose and to increase its stability,[1] the ester may be macerated in a 0.3% aqueous solution of borax, dried and dissolved in tetrachlorethane containing a small quantity of alcohol and petroleum. For 1 k. cellulose acetate the following mixture is given as suitable: Tetrachlorethane 3500 gms., 90% alcohol 350 gms., pure petroleum 18 gms. Non-inflammable sheets may be prepared from this solution. W. Lindsay and the Celluloid Co.[2] stabilize with 1.5% urea in conjunction, preferably with triphenyl phosphate.

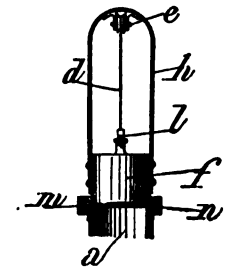
P. Prost and Les Fils Pinay jeune[1] have described an apparatus for effecting the acetylation or nitration of cellulose (paper) in closed vessels. The paper (see Fig. 501) is first corrugated by passage between grooved rolls and the corrugated paper is reeled up loosely to form cylinders in which the corrugations afford free access of liquid to the interior. The treatment of these rolls is effected in earthenware pots, containing the acid, with aluminum hoods. The roll of paper is placed in an aluminum basket which is lowered into the acid. When the paper is saturated with liquid, the basket is raised into the hood and allowed to drain, whilst the cellulose is all the time subjected to the action of the vapors above the liquid. A plate is then slid between the hood and the pot, and the hood, basket and plate are carried on rails to a vessel

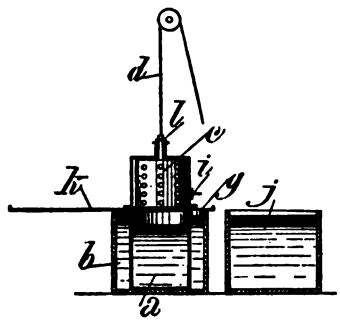
1. D. Young, J. Minuto and F. Seaton-Snowden, E.P. 28848, 1910; abst. J.S.C.I. 1912, **31**, 123; C.A. 1912, **6**, 1526; Jour. Soc. Dyers Col. 1912, **28**, 74; Chem. Tech. Rep. 1912, **36**, 273. F.P. 436900, 1911; abst. Kunst. 1912, **2**, 255; J.S.C.I. 1912, **31**, 428. F.P. 437473, 1911; abst. Kunst. 1912, **2**, 255; J.S.C.I. 1912, **31**, 486. See also E.P. 16133, 1912.

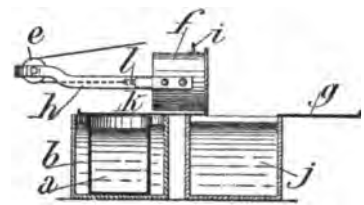
2. U.S.P. 1050065, 1913; abst. J.S.C.I. 1913, **32**, 133; Kunst. 1913, **3**, 218. D.R.P. 263056, 1910; abst. Kunst. 1913, **3**, 375. See also E.P. 10794, 1910; abst. J.S.C.I. 1911, **30**, 679. F.P. 415517, 1910; abst. J.S.C.I. 1910, **29**, 1299; Mon. Sci. 1912, **77**, 9. E.P. 10795, 1910; abst. J.S.C.I. 1911, **30**, 205. F.P. 418518, 1910; abst. J.S.C.I. 1910, **29**, 1299; Mon. Sci. 1912, **77**, 9. U.S.P. 1045990, 1913; abst. J.S.C.I. 1913, **32**, 19; C.A. 1913, **7**, 699. U.S.P. 1067785, 1913; abst. J.S.C.I. 1913, **32**, 823; C.A. 1913, **7**, 3025.











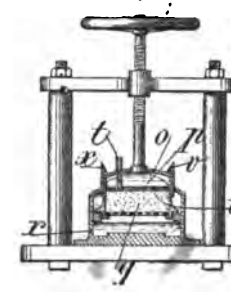


Fig. 501. Acetylation of Cellulose (Cross Method)

of cold water, into which the basket is dropped. The acid pot, meanwhile, is covered with another plate until the hood is charged again. The product is washed, dried and reduced to small particles. These are packed in a perforated shell and impregnated in a press with a liquid containing the following ingredients: Solvent (e. g., alcohol and ether), 1000 c.c.; stannous chloride, 300-400 grms.; camphor, 300-400 grms.; castor oil, 10 grms.; ammonium or barium chloride, 3-10 grms.; sodium chloride, 1-5 grms.; carbon tetrachloride, 20-40 grms.; and lactic acid, 15-50 c.c.

Purification. With the exception of unchanged cellulose or hydrocellulose, and partially or incompletely acetylated cellulose, all the components of the acetating mixture are soluble in cold water, with the possible exception of the diluents added to mollify the reaction or to preserve the structural form of the cellulose used. The usual purification of the acetate from the reacting ingredients is, like the corresponding nitrate, immersion in a large amount of water. But subsequent stabilization by boiling in a slightly acid mixture is not resorted to in cellulose acetate manufacture. Undoubtedly the question of stability of the acetates has not as yet been given the attention it deserves, and probably some of the many difficulties experienced in attempting to produce permanent acetate films for continuous photography is directly traceable to decreased stability induced by the process of acetation. The unacted upon acetate may be directly removed by filtration through cloth after hydration. Before the water for hydration has been added the acetylating mixture will dissolve the cloth, but afterwards it has no dissolving effect upon it. When the acetated cellulose is first precipitated by water it should be immediately disintegrated mechanically to prevent further or local hydrolysis. After washing with water, a gentle boil with alkali is not admissable on account of the further hydrolysis induced by the saponifying effect of the alkali. The acetic acid may be incompletely obtained from the aqueous portion by shaking out with ligroin or petroleum ether and separation by subsequent distillation. In the patented process of Lederer, in which carbon tetrachloride is

used as the restraining and separating agent, it is mixed with the acetylized cellulose until the latter is precipitated when the acetic acid and anhydride are pressed out and separated from the carbon tetrachloride by fractionation.[1] Of course, pouring the product of reaction into water greatly dilutes the esterifying agents, acetic acid and acetic anhydride, the subsequent recovery of which is often further complicated by the presence of restraining agents. The method of purifying cellulose acetates by precipitating the ester by alcohol from its solution in nitrobenzene, chloroform or acetone, is expensive on account of the cost of alcohol, even if denatured alcohol be used, and is further complicated by the tendency of the alcohol to react with the esterizing agent, thereby forming esters, as ethyl acetate.

Bleaching Acetated Cellulose. It is customary to use a bleached cellulose as the starting material, either cotton or tissue paper, but for some uses, as in the manufacture of continuous uninflammable photographic films, it is desirable to produce as nearly optically colorless cellulose acetate as possible.

Assuming the cellulose has received the customary bleach before acetation, there are five subsequent methods offering merit, as follows:

(1). Use of aqueous hydrogen dioxide for the partial or total replacement of the water used in partial hydration, is at the same time an inexpensive, comparatively easy and efficient method. Depending upon the degree of whiteness desired, the water may be partially replaced by either a 10 or 25 volume peroxide solution. During the normal acetylization process, especially where mineral acids as sulfuric are used as catalyzers, there is appreciable darkening of the acetated cellulose, so that the finished ester is not as white as the original cellulose from which produced. The effect of the peroxide is noticeable by the almost instant lightening in color of the acetated mixture, the bleaching effect continuing during the entire partial hydration process.

1. E.P. 20672, 1910; abst. J.S.C.I. 1911, **30**, 854. F.P. 416752, 1910; abst. J.S.C.I. 1910, **29**, 1871; U.S.P. 1061771, 1913; abst. J.S.C.I. 1913, **32**, 597; C.A. 1913, **7**, 2707.

(2). Electrolytically, being applied to the acetated cellulose in the same manner as to unchanged cellulose, except the solution must be of materially less strength. This process has the disadvantage that the solubility of the cellulose acetate is apt to be modified by this treatment, hydrolysis continuing to an appreciable extent, and often the ester sufficiently decomposing so as to be partially insoluble in all acetate solvents.

(3). Hydrolysis of the precipitated and neutralized acetated cellulose by means of sodium peroxide as the saponifying agent, in a similar manner to the saponification process of partial hydration as patented by H. Mork.[1] The sodium peroxide in the presence of water splits into hydrogen dioxide and sodium hydroxide.

(4). Bleaching of the hydrolyzed, washed, neutral acetate by means of potassium permanganate in warm solution, followed by a warm solution of oxalic acid and sulfuric acid. Where acetated cellulose is to be bleached by this method, it is advisable to interrupt the partial hydration process somewhat before the desired solubility is obtained, for the combined action of the oxalic and sulfuric acids at the temperature required carries on hydrolysis. In carrying out this process, therefore, treatment with oxalic and sulfuric acids is carried to the desired solubility in chloroform, acetone or ethyl acetate, the precipitated acetate being then washed until neutral and dried.

(5). The original cellulose may be "blued" before acetation by lightly dyeing with algol, helindone, indanthrene or similar series of colors, or the dyestuff may be dissolved in the acetating bath. When the proportions are right, the acetated cellulose will take on a light bluish color, especially if a fibrous acetate be produced. But a trace of dyestuff is required to produce the light tint.

Recovery of Acetic Anhydride and Acid. The fact that acetated cellulose is soluble in glacial acetic acid and acetic anhydride accounts for the fact that the cotton as it is transformed into ester passes into solution in the acetylating mixture. This is directly opposite to the cellulose nitrates, which

1. F.P. 421864, 1909; abst. J.S.C.I. 1911, 80, 416.

are practically insoluble in ordinary nitrating baths. Acetic anhydride is the most costly of the acetation components, and any method looking to the diminution in amount of anhydride required per unit weight of cellulose acetated must possess great technical interest.

L. Lederer[1] proposes to add sufficient carbon tetrachloride to the acetylating bath so that the combination of acetic acid, anhydride and carbon tetrachloride forms a non-solvent for acetated cellulose. Another point in its favor is that the boiling point of carbon tetrachloride is substantially lower than either acetic acid or anhydride, hence separation by subsequent distillation can be carried on with a higher percentage of solvent recovery in a single distillation. In commercial acetylation, carbon tetrachloride may be added to precipitation of the acetated cellulose at the close of the esterifying process, the precipitated ester being removed by filtration, centrifugal extraction or pressure, and the acetic acid and anhydride recovered and separated from the carbon tetrachloride by subsequent distillation.

In a similar manner benzene or petroleum spirit,[2] or ethyl ether[3] or, in general, any non-solvent of the acetated cellulose is suitable, provided it is at the same time miscible with the constituents of the esterizing bath.

According to the process of H. Dreyfus,[4] in the manufacture of cellulose acetate considerable quantities of acetic

1. U.S.P. 902093, 1908; abst. J.S.C.I. 1908. **27**, 1130. E.P. 26501, 1906; abst. J.S.C.I. 1907, **26**, 430. F.P. 371356, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 79. D.R.P. 185151, 1905; abst. Zts. ang. Chem. 1907, **20**, 1541; Chem. Zentr. 1907, **78**, 498; Jahr. Chem. 1905-08, I, 984.

2. Debauge et Cie, F.P. 450886, 1912; abst. J.S.C.I. 1913, **32**, 596; C.A. 1913, **7**, 3227.

3. International Celluloseester-Gesellschaft, D.R.P. 242289, 1910; abst. C.A. 1912, **6**, 2170; Wagn. Jahr. 1912, II, 17; Kunst. 1913. **3**, 35; Chem. Zts. 1912, **11**, 2798; Chem. Tech. Rep. 1912, **36**, 47; Zts. ang. Chem. 1912, **25**, 286; Chem. Ind. 1912, **35**, 87; Chem. Zentr. 1912, **83**, 298.

4. F.P. 448342, 1912; abst. J.S.C.I. 1913, **32**, 421. In Add. 17674 to F.P. 448342 (abst. C.A. 1914, **38**, 2805) is described a process of manufacture of fatty acid anhydrides and fatty acid chlorides, strongly cooled salts such as sodium acetate are gradually mixed with such amounts of sulfur trioxide or chlorosulfonic acid, that one molecule each of acetic acid and acetic anhydride result.

acid may be recovered for future use. This acid is either partially neutralised, or else mixed with metallic acetates, and treated with reagents capable of producing acetic anhydride, such as sulfur chloride, sulfuryl chloride, chlorine and sulfur, chlorine and sulfur dioxide, salts of chlorosulfonic acid, halogen compounds of phosphorus, etc. The reagents may be employed in such proportions that a mixture of acetic anhydride and acetic acid results, suitable for re-employment as an acetylating agent, either directly or after fractional distillation. If the metallic acetate be omitted, similar mixtures of acetyl chloride and acetic acid may be obtained for the same purpose.

The acetic acid from the acetating bath and from the wash waters may be first neutralized by means of sodium carbonate, quicklime or calcium carbonate, evaporated to crystallization, and the sodium acetate or calcium acetate used directly for acetic acid or acetone manufacture. In a recently patented process [1] magnesia is specified as especially valuable for purposes of neutralization.

Acetates of the Carbohydrates. The intimate chemical relationships between cellulose and the water-soluble carbohydrates, and the fact, recently established by R. Willstaetter and L. Zechmeister,[2] that cotton cellulose may be directly

1. D.R.P. 260984, 1912; abst. C.A. 1913, **7**, 3228.

2. Ber. 1913, **46**, 2401; abst. J.S.C.I. 1913, **32**, 822; C.A. 1913, **7**, 3412; J.C.S. 1913, **104**, i, 955; Jour. Dyers Col. 1913, **29**, 326; Bull. Soc. Chim. 1913, **14**, 1354; Chem. Zentr. 1913, II, 1209. They found that, while ordinary concentrated hydrochloric acid (sp. gr. 1.19) and even acid of sp. gr. 1.196 are not capable of dissolving cellulose, complete solution can be effected rapidly in fuming hydrochloric acid of sp. gr. above 1.2; acid of about 41 per cent. concentration (sp. gr. 1.209—1.212 at 15°) is preferably used. Cotton or filter paper dissolves in about 10 seconds to a clear solution in acid of sp. gr. 1.209. In order to obtain concentrated solutions, the cotton is immersed in and kneaded with the acid. Solutions containing 7, 12—13, and about 15 per cent. of cellulose were obtained with acid of sp. gr. 1.204, 1.209 and 1.212 respectively. The solutions are colorless and clear at first, but after 1 day a slight flocculent precipitate frequently appears, and after several days the liquid acquires a yellow color, and a dark brown substance begins to separate. Solutions of dextrose in hydrochloric acid behave in a similar manner. If the solution be diluted within 30 30-45 minutes after preparation, a form of cellulose is precipitated quantitatively, and the solution has no cupric-reducing power even after prolonged boiling. The cellulose precipitated by water is plastic and becomes

and quantitatively hydrolyzed into dextrose, has added new interest to acetated saccharides. The earlier work of G. Bouchardat on the di-, tri- and hexa-acetates of dulcite [1] and tetra- and hexa-acetyl mannit,[2] and the work of A. Gautier on the glucose acetates,[3] have been extended by many subsequent investigations, some of the products obtained being of interest as possible softening agents to be used in conjunction with the cellulose esters.

Fisher and Armstrong [4] and R. Foerg [5] prepared hepta-

horny on drying. With iodine solution it gives a dark coloration which is less characteristic than that obtained with cellulose hydrate, but resists washing better than that obtained with Girard's hydrocellulose (J.S.C.I. 1882, 1, 159, 316). On more prolonged standing of the hydrochloric acid solution, the cellulose is hydrolyzed and the solution acquires reducing properties. Hydrochloric acid presents a great advantage over sulfuric acid as an agent for hydrolyzing cellulose in that hydrolysis is complete in 1-2 days in the cold and can be followed from beginning to end with the polarimeter. A yield of 95-96 per cent. of the theoretical quantity of dextrose (determined with the polarimeter and by reduction of Fehlings solution) is obtained, and the problem of the quantitative saccharification of cellulose (and of wood) can hence be regarded as solved. The hydrochloric acid solutions of cellulose are optically inactive at first. With a solution containing 1 grm. of cellulose in 100 cc., optical activity was first observed after 1 hour and then increased up to the rotatory power of dextrose in the course of 24-48 hours according to the acid concentration. Direct experiments showed that the rotatory power of dextrose is enormously increased when it is dissovled in concentrated hydrochloric acid; an increase of $[\alpha]d$ from 53° to 180° was observed. The rotatory power of the hydrochloric acid cellulose solution does not increase uniformly throughout the hydrolysis; after a time it increases less rapidly, then remains practically constant, and finally again increases steadily. This indicates that an intermediate compound, probably cellobiose, is formed at first and is subsequently hydrolyzed to dextrose. In addition to cotton and filter-paper, pine wood also dissolves rapidly in fuming hydrochloric acid, leaving an insoluble residue (30 per cent.) of lignin-substances, which are in a purer form than when sulfuric acid is used. Concentrated hydriodic acid does not dissolve cotton in the cold, but 66 per cent. hydrobromic acid (sp. gr. 1.78) dissolves it readily and completely even at 0°. Hydrofluoric acid of 70-75 per cent. concentration gelatinizes cotton and rapidly dissolves it.

1. G. Bouchardat. Compt. rend. 1872, 74, 665; abst. Bull. Soc. Chim. 1872, (2), 17, 194; Zts. Chem. 1871, 675; Jahr. Chem. 1872, 773; J.C.S. 1872, 25, 400; Chem. Centr. 1872, 246.

2. G. Bouchardat, Ann. Chim. Phys, 1875, (5), 6, 100; abst. Jahr. Chem. 1875, 790; J.C.S. 1875, 28, 443; Chem. Centr. 1875, 130.

3. Bull. Soc. Chim. 1874, (2), 22, 145; abst. Jahr. Chem. 1874, 883; Chem. Centr. 1874, 707.

4. Fischer and E. Armstrong. Ber. 1901, 34, 2885; abst. Jahr. Chem. 1901, 847; Sitzungsber, Akad. Wiss. Berlin, 1901, 7, 123;

chloracetylmaltose, Koenigs and Knorr[1] methylmaltoside heptacetate, and A. Bodart[2] heptacetylchlorlactose and pentacetylglucose, but they were either deliquescent, amorphous, unstable or indefinitely characterized. The tetracetylmethylglucosides of E. Fischer were further investigated by J. von Charante,[3] and the chloracetyl glycogens of E. von Kraffl-Lenz,[4] but they have apparently no technical interest. R. Kremann[5] has measured the velocity of hydrolysis of the pentacetyl- and tetracetylchloro-derivatives of dextrose and galactose, of tetracetylgalactose, and of the octacetyl-derivatives of lactose, maltose and saccharose, and studied their products of chlorination and nitration. Pentacetyldextrose, octacetyldiglucose, and their derivatives have been described in detail by Herzfeld,[6] and by E. Erwig and W. Koenigs,[7] Many of these derivatives have been patented as camphor substitutes and plastic-inducing bodies in conjunction with cellulose nitrate, especially acetylated derivatives of glucose, levulose and lactose, the various acetates of saccharose, and the tartrates of glucose and lactose.

Cellulose Formate (Formylcellulose). (8) It is only

Chem. Centr. 1901, II, 981; Bull. Soc. Chim. 1902, **28**, 128; J.C.S. 1901, **80**, i, 189.

5. Monatsh. 1902, **23**, (1), 44; abst. J.S.C.I. 1902, **21**, 506; Zts. ang. Chem. 1901, **14**, 1210; Wien. Akad. Ber. 110, II B, 1054; J.C.S. 1902, **82**, i, 347; Chem. Centr. 1902, I, 861; Jahr. Chem. 1901, 877.

1. W. Koenigs and E. Knorr, Ber. 1901, **34**, 957; abst. Jahr. Chem. 1901, 848; Chem. Centr. 1901, I, 1095; Bull. Soc. Chim. 1901, **28**, 314; J.C.S. 1901, **80**, i, 369.

2. Monatsh. 1902, **23**, 1; abst. J.S.C.I. 1902, **21**, 506; J.C.S. 1902, **82**, i, 347; Bull. Soc. Chim. 1903, (3), **30**, 551; Chem. Centr. 1902, **73**, I, 803; Zts. ang. Chem. 1901, **14**, 1210.

3. Rec. trav. Chim. 1902, **21**, 42; abst. Bull. Soc. Chim. 1902, (3), **28**, 482.

4. Bull. Soc. Chim. 1906, (3), **36**, 456; abst. Zts. Physik. C. 1905, **46**, 293; Jahr. Chem. 1905-08, II, 952.

5. Monatsh. 1902, **23**, (5), 479; abst. J.S.C.I. 1902, **21**, 996; Bull. Soc. Chim. 1903, (3), **30**, 310; J.C.S. 1902, **88**, i, 712; Jahr. Chem. 1902, 227, 1011; Chem. Centr. 1902, II, 512.

6. Ber. 1880, **13**, 266; abst. Chem. Centr. 1890, 757; Jahr. Chem. 1880, 1011; Bull. Soc. Chim. 1881, **1**, 250; J.C.S. 1880, **38**, 619.

7. Ber. 1889, **22**, 1464; abst. Chem. Centr. 1890, 757; Jahr. Chem. 1890, 3132; Bull. Soc. Chim. 1890, **3**, 12; J.C.S. 1890, **58**, 732.

8. For resume of formylcellulose, containing 334 bibliographic

within the past ten years that the cellulose formates as industrial possibilities have been brought to the attention of investigators. The recent marked reduction in the cost of producing formic acid, and the fact that no counterpart of acetic anhydride—the most expensive ingredient in acetating cellulose—is required in their preparation, have caused great interest in these esters to be displayed within the past few years. The cellulose formates differ greatly from the corresponding acetic esters, just as formic acid or any first member of an homologous series differs from the higher members in that series. This difference is especially noticeable in reactivity and solubility.

Transformation of cellulose into its formic acid esters has been found to be a much more difficult operation than the formation of the nitro- or acetyl- celluloses. These difficulties are partly founded upon the more energetic reactivity of formic acid, which must be regarded as one of the most powerful organic acids as regards the esterification process. Not only does the cellulose complex undergo changes in the hydroxyl groups, but if the usual precautions are not observed, the cellulose complex is attacked, leading to the formation of an octoformylcellobiose (cellobiose octoformate). In contradistinction, acetylation, even in the presence of the strongest dehydrating agents and catalysts like sulfuric acid, always shows the character of a progressive esterification. The formates of cellulose, like those of glycerol, are very sensitive to heat, this being a general property of the formates of polybasic alcohols. It is known that the glyceryl formates upon saponification yield allyl alcohol, from which it has been assumed that the cellulose formates behave in an analogous manner.

Whereas acetic acid acts only in the form of its anhydride and in the presence of dehydrating and hydrolyzing agents upon cellulose, formic acid of not over 90% strength in the presence of a dehydrating agent is capable of esterifying many

references in 65 notes, see E. Worden and L. Rutstein, Kunst. 1912, 2, 325-8; abst. C.A. 1912, 6, 3329; Chem. Tech. Rep. 1912, 86, 562. See also Caout. et Guttap. 1913, 10, 6897, Kunst. 1913, 3, 352. E. Worden, Chem. Engr. 1913, 17, 26; abst. C.A. 1913, 7, 2304.

forms of cellulose. Furthermore, the process may be carried on at much lower temperatures than is necessary in the case of acetic acid. The reactive esterification velocity of formic acid is given as 61.69, that of acetic acid being 44.8; the absolute velocity is 96.4, against 65.38 for acetic acid, values which corroborate the results of Mentschutkin, viz., 100.71. From this it follows that the limit reaction for formic acid is much wider than for acetic acid, the latter being 81.46. Organic acid esterification is always an endothermic process. Pressure and temperature also play an important role in the preparation of formylcelluloses, the limit of esterification for an acid of 60% at reduced (20 mm.) pressure and for a temperature of 110 being 80% without catalysts and dehydrating agents. At atmospheric pressure esterification velocity increases with the temperature when relatively diluted solutions are used, the esterification limits increasing and decreasing in indirect proportion.

The mechanics of formylation of cellulose is not directly comparable with the process of nitration, for in the latter reaction the cellulose aggregate is not appreciably attacked, although strong acids are employed and high temperatures maintained. With fuming nitric acid, concentrated sulfuric acid and phosphorus pentoxide, dodecanitrates are obtained which are true esters. In formylation, however, the initial action of the formic acid is a depolymerization of the cellulose followed by esterification of the single molecule under formation of a tri-ester, or the reaction is extended to the ketonic or aldehydic groups of the molecule.

In the usual process of esterification corresponding to the reversible reaction of alcohol plus acid equals ester plus water, dehydrating agents change the equilibrium in favor of the ester. Vieille has shown in nitration up to 450 parts of dehydrating agent may be consumed for 3 parts of acid without a material change in the titer of the bath. When using formic acid, however, it is impossible to proceed in the same manner, because the majority of the dehydrating agents probably also act upon the acid, transforming the same into carbon monoxide and water. Gaseous HCl alone appears

not to be possessed of this unfavorable influence, and it is therefore a peculiar suitable dehydrating agent for formylation. It is, nevertheless, necessary to observe caution, especially when the temperature of formylation becomes elevated, because the esterification is thereby greatly accelerated and can be regulated only with difficulty. Velocity of reaction increases with rise of temperature, and is at 200° about 22000 times greater than at 70°. In order to decrease the velocity of esterification in such cases, inert substances like benzene, benzine, chloroform, carbon tetrachloride and acetic acid are used as diluents. Dehydrating agents, especially the more powerful of the inorganic acids, tend to partially saponify the esters as produced, when present in excess. This drawback is obviated by the addition of salts of these acids, which still act as dehydrating agents. If the action of the formic acid be too far progressed and the cellulose moleculte strongly attacked, an advantageous addition is a powerful polymerizing agent such as formaldehyde. The use of anhydrous formates as dehydrating agents is successful at low temperatures, but with the higher temperatures barium formate alone may be used, the other formates decomposing into CO and water.

Generally speaking, the formates may be considered as analogues of the cellulose acetates, although Cross and Bevan have pointed out that the original cellulose molecule undergoes a change by the action of the formic acid whereby another alcoholic hydroxyl enters into the reaction. A characteristic of formylated cellulose is solubility in 20% solutions of the alkali and alkaline-earth sulfocyanides. In contradistinction to the acetate, the formates of cellulose can be obtained only with great difficulty in the fibrous form, i. e., without apparent change in the structure of the cellulose. In the presence of liquids in which the formylcellulose is insoluble, such as benzene, benzine, and carbon tetrachloride, the fibrous structure is destroyed and a thick syrup obtained.

Many of the solvents of the cellulose acetates do not dissolve the formic esters, lactic acid being the notable exception. The partial hydration of cellulose acetate, resulting in the formation of a series of technically very valuable products in

that they possess considerable flexibility and tensile strength in addition to dissolving in acetone and other readily available and inexpensive solvents, finds no analogue in the formates.

The cellulose formates may be prepared by many of the general methods applicable to acetic ester formation, and from hydrocellulose or other modified cellulose without resort to esterizing agents, cellulose hydrate [1] and the waste from artificial silk manufacture.[2] Denitrated nitrocellulose filaments and viscose silk waste have been found especially suitable. As with the corresponding acetates, much time and experimentation has been given to the selection of suitable hydrolyzing agents, and the conditions under which they are most dependable. For the formylation of natural cellulose (cotton), the most important advocated have been sulfuric acid,[3] zinc

1. U.S.P. 953677, 955082, 1910; abst. J.S.C.I. 1910, **29**, 557; Mon. Sci. 1910, (4), **73**, 131. E.P. 17036, 1909; abst. J.S.C.I. 1910, **29**, 1005. F.P. 405293, 1909; abst. J.S.C.I. 1910, **29**, 417; Mon. Sci. 1910, (4), **73**, 171; Chem. Tech. Rep. 1910, **34**, 75. D.R.P. 219162, 219163, 1907; abst. Jahr. Chem. 1910, I, 426; Zts. ang. Chem. 1910, **23**, 768; Chem. Ind. 1910, **33**, 186; Wagn. Jahr. 1910, **56**, II, 433; Mon. Sci. 1914, **81**, 80; Chem. Zts. 1910, **9**, 1986, 1988. Aust. P. 45765, 1909. Hung. Anm. N.-952, July 21, 1909. It. P. 103978, 1909. Belg. P. 198984, 198985, 217837, 1907.

2. U.S.P. 1046729, 1912; 1061977, 1913; abst. J.S.C.I. 1913, **32**, 653; C.A. 1913, 7, 700, 2471; Mon. Sci. 1914, **80**, 23. E.P. 15700, 1910; 6241, 1911; abst. J.S.C.I. 1910, **29**, 1199; 1912, **31**, 279; C.A. 1911, **5**, 2723; 1912, **6**, 2529; Chem. Tech. Rep. 1912, **36**, 532; F.P. 420856, 1910; abst. J.S.C.I. 1911, **30**, 279; Mon. Sci. 1913, **78**, 113. First Add. to F.P. 420856, dated Mar. 13, 1911; abst. J.S.C.I. 1911, **30**, 1050. D.R.P. 233589, 1909; abst. Zts. ang. Chem. 1911, **24**, 860; Chem. Zts. 1912, **11**, 2733; C.A. 1912, **6**, 2169, 2170, 2315; Chem. Zentr. 1911, I, 1333; Chem. Tech. Rep. 1912, **36**, 675; Wagn. Jahr. 1912, II, 18. D.R.P. 254093, 1910, being Add. to D.R.P. 233589, 1909; abst. Chem. Zentr. 1913, **84**, 83; Chem. Tech. Rep. 1912, **36**, 693; Kunst. 1913, **3**, 52, 260; C.A. 1913, **7**, 1288. Belg. P. 233792, 234433, 1911; 229046, 1910. Aust. P. 49177, 54819, 57421, 60447; abst. Kunst. 1912, **2**, 456; 1913, **3**, 218, 395. Swiss P. 53585, 1910. Hung. Anm. G.-3306, Mar. 13, 1911. Can. P. 133197, 1911. The formic acid employed is the ordinary formic acid of commerce, of about 96% strength by weight. The cellulose hydrates will dissolve in this formic acid at ordinary room temperatures, but a temperature of 40-50° is preferable. At higher temperatures the solution is more rapidly formed, but is more thinly flowing.

3. E.P. 2511, 1907; abst. J.S.C.I. 1907, **26**, 634; Jour. Soc. Dyers, 1907, **23**, 215. F.P. 376262, 1907; abst. J.S.C.I. 1907, **26**, 988; Mon. Sci. 1908, (4), **68**, 87. D.R.P. 189836, 189837, 1908; abst. Zts. ang. Chem. 1908, **21**, 268; Jahr. Chem. 1905-08, II, 983; J.C.S. 1908, **94**, i, 321; Chem. Ind. 1907, **30**, 617; Wagn. Jahr. 1907,

chloride and sulfuric acid,[1] gaseous hydrochloric acid,[2] other halogens [3] combination of sulfuric and hydrochloric acids in the form of sulfuryl chloride, pyrosulfuryl chloride,[4] and chlorosulfonic acids.[5] Certain aliphatic and aromatic sulfonic acids and esters which split off sulfuric acid, such as ethylsulfuric acid [6] and the phenolsulfonic acids and sulfonates.[7] The cellulose, if desired, may also be dyed before formylation. The phosphoformates of the Vereinigte Glanzstoff Fabriken Akt. are said to be especially valuable when com-

II, 400. D.R.P. 189836 specifies formylation in the presence of sulfuric acid, while D.R.P. 189837 claims the use of gaseous HCl, 2-4 parts being required for 20-30 parts of cellulose.

1. U.S.P. 953677, 955082, 1910; abst. J.S.C.I. 1910, **29**, 557; Mon. Sci. 1910, (4), **73**, 131. E.P. 17036, 1909; abst. J.S.C.I. 1910, **29**, 1005. F.P. 405293, 1909; abst. J.S.C.I. 1910, **29**, 417; Mon. Sci. 1910, (4), **73**, 171; Chem. Tech. Rep. 1910, **34**, 75. D.R.P. 219162, 219163, 1907; abst. Jahr. Chem. 1910, I, 426; Zts. ang. Chem. 1910, **23**, 768; Chem. Ind. 1910, **33**, 186; Wagn. Jahr. 1910, 56, II, 433; Chem. Zts. 1910, **9**, 1986, 1988. Aust. P. 45765, 1909. Hung. Anm. N.-952. July 21, 1909. It. P. 103978, 1909. Belg. P. 198984, 198985, 1907; 217837, 1909.

2. E.P. 2511, 1907; abst. J.S.C.I. 1907, **26**, 634; Jour. Soc. Dyers, 1907, **23**, 215. F.P. 376262, 1907; abst. J.S.C.I. 1907, **26**, 988; Mon. Sci. 1908, (4), **68**, 87. D.R.P. 189836, 189837, 1908; abst. Zts. ang. Chem. 1908, **21**, 268; Jahr. Chem. 1905-08, II, 983; J.C.S. 1908, **94**, i, 321; Chem. Ind. 1907, **30**, 617.

3. E.P. 22237, 1911; F.P. 435507, 1911; abst. Mon. Sci. 1913, **78**, 133. Belg. P. 239564, 1911, abst. J.S.C.I. 1912, **31**, 279, 329.

4. U.S.P. 1051165, 1913; abst. Kunst. 1913, **3**, 275; J.S.C.I. 1913, **32**, 192. E.P. 24382, 1910; abst. J.S.C.I. 1911, **30**, 616; C.A. 1911, **5**, 3157. F.P. 423197, 1910; abst. J.S.C.I 1911, **30**, 615; Chem. Tech. Rep. 1911, **35**, 307. Swiss P. 54497, 1910. Belg. P. 229995, 1910.

O. Bonhoeffer, H. Guntrum and Farb. v. Bayer & Co., D.R.P. 237765, 1909 (zinc chloride and sulfuryl chloride); and D.R.P. 237766, 1909 (zinc chloride and chlorosulfonic acid). U.S.P. 1093247, 1914; F.P. 422542, 1910; abst. J.S.C.I. 1911, **30**, 532; 1914, **33**, 546.

5. F.P. 430606, 1911; abst. J.S.C.I. 1911, **30**, 1375; Mon. Sci. 1913, **78**, 127.

6. U.S.P. 994738, 1911; abst. J.S.C.I. 1911. **30**, 888. E.P. 1556, 1911; abst. J.S.C.I 1911, **30**, 1236, 1309; C.A. 1912, **6**, 1853. F.P. 427445, 1911; abst. J.S.C.I. 1911, **30**, 1051. D.R.P. 237210, 1910; abst. Zts. ang. Chem. 1911, **24**, 1837; Chem. Zentr. 1911, **82**, 497; Chem. Ind. 1911, **34**, 535. Belg. P. 233876, 1911. Aust. Anm. A.-2376, Mar. 16, 1911; abst. Chem. Ztg. 1912, **36**, 252.

7. E.P. 29246, 1910; 309, 1911. F.P. 423774, 1910; abst. Mon. Sci. 1913, **78**, 31. F.P. 424621, 1911; D.R.P. 249535, 1910; Aust. P. 54512, 1912. Hung. P. 3096. 1910. Swiss P. 53777; Belg. P. 231853, 1911; Can. P. 134164, 1911, abst. J.S.C.I. 1911, **30**, 484, 615, 741, 888; C.A. 1911, **5**, 3340; 1912, **6**, 3188; Kunst. 1912, **2**, 255, 393.

bined with certain plastic inducing bodies such as triphenyl phosphate.

C. Cross and E. Bevan [1] have called attention to the fact that in addition to the normal replacement of alcoholic hydroxyl groups of the O.COH group, in cellulose, formic acid may attack cellulose by hydrolysis or condensation, either separately or concurrently, or the acid may react through its carbonyl oxygen atom, giving rise to complexes, thus:

$$\begin{matrix} H \\ HO \end{matrix}\!\!>\!\!CO + \begin{matrix} H.X \\ H.Y \end{matrix} = H_2O + \begin{matrix} H \\ HO \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} X \\ Y \end{matrix}$$

Their results obtained by the direct interaction of formic acid on cellulose, and also in the presence of condensing agents are reconcilable with the views that the products are simple esters of a normal cellulose.[2]

1. J.C.S. 1911, **99**, 1450-1456; abst. J.S.C.I. 1911, **30**, 1008; C.A. 1911, **5**, 3568; Chem. Zentr. 1911, **82**, II, 855-6; Zts. ang. Chem. 1911, **24**, 2084; Chem. News 1911, **103**, 295.

2. They found the viscous solutions obtained may be precipitated by water or allowed to evaporate on a glass surface to a transparent film. The precipitated substance when washed and dried in the air was soluble in pyridine and nitrobenzene and in a 20% solution of potassium or ammonium thiocyanate. It retains 8-9% of moisture, and upon saponification yields figures corresponding to cellulose diformate, but on analysis to cellulose monoformate. After four months storage in a closed bottle, the material had a decided acid reaction due to the liberation of formic acid, and upon distillation of the product with water, formic acid calculated in amount to one molecule on the diformate was obtained. The authors conclude, therefore, that the product is a monoformate of a modified cellulose, the second molecule of acid obtained by saponification being in reality derived from the cellulose by the action of the alkali. Upon acetylation of the original formate, a cellulose diacetylmonoformate was obtained. The cellulose residue obtained from the saponification of the original formate shows signs of profound constitutional modification, containing an unusually high percentage of hydrogen, and on acetylation giving an abnormally high yield of acetylated product containing more than the usual three molecules of acetic acid characteristic of cellulose triacetate. Examination of the film prepared from evaporation of a formate solution gave indications that it was essentially a modified cellulose, insoluble in pyridine and carrying 13-16% of hygroscopic moisture. On prolonged boiling with sodium hydroxide solution a progressive splitting off of acid products was observed. When cellulose is treated with formic acid in presence of a catalyst as zinc chloride or phosphoric acid, a viscous solution forms, and upon pouring into water, the latter retains in solution a certain proportion of modified cellulose products. The aggregate gain in weight of the insoluble and soluble products is relatively low, and the insoluble portion gives upon saponification values in excess of that corresponding to its elementary composition regarded as an ester.

E. Berl and W. Smith have shown [1] that cellulose monoformate may be prepared by the action of substantially absolute formic acid in the presence of 5% by weight of sulfuric acid, but they were unable to prepare technically useful esters. R. Woodbridge [2] found that when formic acid of specific gravity of 1.20 is substituted for the anhydrous compound, no formate results, while on the other hand, where the most concentrated acid is employed, filter paper dried at 100° is as efficient starting material as the hydrocellulose prepared according to the method of Girard. In his preferred method 18 parts dried filter paper is treated with 100 grams formic acid of sp. gr. 1.22 and 10 gm. sulfuric acid for 16 hours at 30°-35°. After thinning with more formic acid, the heavy viscous mass is filtered from unacted upon cellulose, precipitated in a large bulk of water, washed to neutralization and dried at a low temperature. The product thus obtained was found to be soluble in formic acid, zinc chloride, insoluble in methyl, ethyl or amyl alcohols, acetone, chloroform, carbon tetrachloride, acetylene tetrachloride, ethyl ace-

In connection with the solubility statements of formylated cellulose in the alkaline thiocyanates, A. Dubosc (Caout. et Gutta P. 1913, 10, 6895; abst. C.A. 1913, 7, 2112; Kunst. 1913, 3, 155) has called attention to additional investigation of the solubility of alkalicellulose in alkali thiocyanates as made by himself in 1905 (Bull. Soc. Ind. Rouen, 1905, 318), and to his conclusions that alkaline thiocyanates are not simple cellulose formate solvents, the solvent action being due to or accompanied by a double decomposition, the CHOO being replaced by CNS, with probable formation of other compounds. If a mixture of sodium hydroxide 50, sodium carbonate 30, cellulose 100 and water 1000 parts be treated with a thiocyanate easily decomposable by heat, as the ammonium salt or HCNS. at a pressure of 2.5 atmospheres for 3 or 4 hours, gelatinization and subsequent solution rapidly ensues with the formation of a new ester—cellulose thiocyanate.

Zts. ang. Chem. 1913, 26, 89; abst. J.S.C.I. 1913, 32, 227; C.A. 1913, 7, 1969. Gummi Ztg. Celluloid Industrie Suppl. 1913, 8, 69; abst. Kunst. 1913, 3, 154.

1. Ber. 1907, 40, 903-908; abst. J.C.S. 1908, 94, i, 505; J.S.C.I. 1908, 27, 534; C.A. 1909, 3, 838.

2. J.A.C.S. 1909, 31, 1070; abst. J.C.S. 1909, 96, i, 768; Bull. Soc. Chim. 1910, (4), 8, 823; Zts. ang. Chem. 1910, 23, 144; Jahr. Chem. 1909, 386; J.S.C.I. 1909, 28, 1061; C.A. 1910, 4, 667. He was unable to prepare a fibrous cellulose formate, his experiments indicating that the addition of even a small amount of neutral solvent practically stops acidylation, while if the quantity of diluent is reduced to a point where some formylation takes place, the product then dissolves in the reacting mixture.

tate, amyl acetate, nitrobenzene, aniline, or dilute acetic, sulfuric or hydrochloric acids. The insolubility of the formic ester in acetylene tetrachloride is a qualitative distinction and separation from the acetate. Saponification yielded 23.1% formic acid, the monoformate requiring 24.2%.

The recuperation of formic acid from a mixture with sulfuric or other mineral acid presents difficulties, and the solution of the cellulose is subjected to sufficiently speedy decomposition owing to the presence of the comparatively large amounts of energetic mineral acid. Where the ultimate product is required to possess the maximum strength, as when used for artificial silk filaments, these objections have weight. The Nitritfabrik Akt.[1] have devised a process of rendering cellulose soluble in formic acid in order to obtain formylated cellulose solutions applicable for spinning, by first forming hydrocellulose,[2] washing free from inorganic acid and drying,

1. U.S.P. 953677 955082, 1910; abst. J.S.C.I. 1910, **29**, 557; Mon. Sci. 1910, (4), **73**, 131. E.P. 17036, 1909; abst. J.S.C.I. 1910, **29**, 1005. F.P. 405293, 1909; abst. J.S.C.I. 1910, **29**, 417; Mon. Sci. 1910, (4), **73**, 171; Chem. Tech. Rep. 1910, **34**, 75. D.R.P. 219162, 219163, 1907; abst. Jahr. Chem. 1910, I, 426; Zts. ang. Chem. 1910, **23**, 763; Chem. Ind. 1910, **33**, 186; Wagn. Jahr. 1910, **56**, II, 433; Chem. Zts. 1910, **9**, 1986, 1988. Aust. P. 45765, 1909. Hung. Anm. N.-952, July 21, 1909. It. P. 103978, 1909. Belg. P. 198984, 198985, 1907; 217837, 1909.

2. In their method 1 part by weight of cotton is placed in 15 parts by weight of sulfuric acid 55° Be., until a thick, tenacious paste is formed. This is precipitated in water, washed and dried. The product thus obtained is dissolved in formic acid of 95-98% strength, when it is ready for use. Or, 50 parts by weight of zinc chloride are dissolved in 40 parts of dilute formic acid (30-40% formic acid), 5-10 parts by weight of cellulose being impregnated with this solution, which dissolves in speed according to the temperature. The cellulose is then precipitated by water, washed, dried and dissolved in formic acid. Or 30 parts zinc chloride may be dissolved in 100 parts of concentrated formic acid and 10-20 parts of cotton impregnated with the solution. The cellulose dissolves gradually at room temperature, more quickly at elevated temperatures, forming solutions of cellulose mono-, di- or tri-formates. In this modification of the process, where zinc chloride is used as the esterifying agent (U.S.P. 955082, 1910; D.R.P. 219163, 1907; Aust. P. 45765), the simultaneous action of the zinc chloride and formic acid is explained by the following equation, assuming the formation of cellulose monoformate:

$$C_6H_{10}O_5 + HCOOH + xZnCl_2 = C_6H_9O_4.O.HCO + xZnCl_2 + H_2O.$$

The cellulose formate thus obtained may be freed from zinc chloride by washing with water, and may then be dissolved in formic acid to give a solution of the formate free from zinc chloride.

when the dry product may be directly formylated by solution in formic acid and zinc chloride, with the elimination, the patentees claim, of the decomposition phenomena referred to above. In their preferred method 50 parts zinc chloride is dissolved in 40 parts dilute formic acid, cotton or cellulose being impregnated with this solution. After the cellulose has passed into solution, it is precipitated in water, washed free from zinc chloride and dried. The dry product is dissolved in formic acid, forming a solution utilizable for artificial silk formation.

H. Deming [1] prefers dry hydrochloric acid gas, his method being to saturate 3 gm. of filter paper in 100 c.c. of formic acid which had been previously saturated at room temperature with dry HCl gas. The product was precipitated after four hours, and found slowly soluble in formic acid, slightly soluble in pyridine, and insoluble in the other reagents which dissolve the cellulose acetates. If allowed to remain in the acid liquid 24 hours before precipitating, the ester first formed is saponified to a modified cellulose. Instead of hydrochloric acid, the halogens in combination among themselves have been found suitable in the hands of the Actien-Ges. fur Anilin-Fabrikation [2] chlorine, bromine or [3] iodine monochloride, iodine trichloride, iodine monobromide or bromine chloride being specified.

The energetic action of sulfuric or hydrochloric acids may be modified without materially decreasing their deficiency by

According to the statements of the patentee, the formic acid solution may be used directly for artificial silk formation by simply forcing the filtered solution through minute orifices into water as the coagulating medium, the solvent being recovered from the water by direct distillation. In this connection attention is called to the fact that the boiling point of formic acid and of water are only about one degree apart.

1. J.A.C.S. 1911, **33**, 1519; abst. J.S.C.I. 1911, **30**, 1111; J.C.S. 1911, **100**, i, 771; C.A. 1911, **5**, 3678; Chem. Zentr. 1911, **82**, 1434. He found that a mixture of 30 cc. formic acid sp. gr. 1.22, 70 cc. hydrochloric acid sp. gr. 1.40 and 10 gm. calcium chloride will dissolve 1.5 gm. cellulose within 15 minutes, while a mixture of the two acids alone will affect no solution in 24 hours.

2. E.P. 22237, 1911; abst. J.S.C.I. 1912, **31**, 279. See also their E.P. 1156, 1914; F.P. 461058, 1913.

3. F.P. 435507, 1911; Belg. P. 239564, 1911; abst. J.S.C.I. 1912, **31**, 329.

combining the two, sulfuryl chloride with [1] or without [2] zinc chloride being used. In the latter method, chlorides of sulfuric acid such as SO_2OHCl, SO_2Cl_2, and $S_2O_5Cl_2$ are employed as indicated in the following example:[3] 100 parts by weight of cellulose—previously preferably dried rapidly artificially at 105°—are soaked with 500 parts or more of formic acid of 98%-100% strength and 2-3 parts of sulfuryl chloride, solution being complete in 1 or 2 days. Where zinc chloride is used, either sulfuryl chloride [4] or chlorosulfonic acid [5] is advocated in addition to formic acid. The white voluminous mass obtained by precipitation of the formylated mass in a large volume of water is soluble in formic acid, zinc chloride solution, and is distinguished from the formyl cellulose compounds of the older art by being soluble in pyridine. The patentees state that upon evaporation of solutions of the formyl celluloses, a colorless and translucent flexible film remains. In the method of C. E. Dreyfus [6] cellulose esters can be produced even in the cold by the action of formic

1. D.R.P. 237765. 237766, 1909; abst. Wagn. Jahr. 1911, II, 420. E.P. 24980, 1910; F.P. 422542, 1910; abst. Mon. Sci. 1913, 78, 116. Aust. P. 8776, Nov. 11, 1910; abst. J.S.C.I. 1911, 30, 532, 1112; C.A. 1912, 6, 1672. Aust. P. 52289; abst. Kunst. 1913, 3, 274.

2. E.P. 24382, 1910; F.P. 423197, 1910; abst. Mon. Sci. 1913, 78, 117. Swiss P. 54497, 1910. Belg. P. 229995, 1910; abst. J.S.C.I. 1911, 30, 615, 616; C.A. 1911, 5, 3157; Chem. Tech. Rep. 1911, 35, 307.

3. Example 3: E.P. 24382, 1910. See also Internationale Celluloseester Ges. D.R. Anm. 22h. J. 14823, of July 4, 1912, and Addition thereto, being D.R. Anm. 22h. J. 15495, of Feb. 25, 1913; abst. Kunst. 1913, 3, 300, 318.

4. D.R.P. 237765, 1909. The method given is to make a mixture of 100 parts of 98-100% formic acid and 10 parts sulfuryl chloride, into which is immersed 20 parts of dry cotton. The reaction commences immediately, and is hastened by raising the temperature to 30°. There is gradually formed a viscous solution of formylcellulose which may be precipitated by the addition of a large bulk of water. Or, a mixture of 100 parts 95% formic acid, 5 parts zinc chloride and 10 parts sulfuryl chloride is made, and 20 parts of cotton immersed in the mixture. After standing for some hours, a highly viscous colorless solution of formylcellulose results. Hydrocellulose and oxycellulose, the patentee states, acts in a similar manner. Where the formylating temperature is kept lower and the catalyzing material reduced in quantity higher formylated products are formed. Chlorosulfonic acids are also specified.

5. D.R.P. 237766, 1909.

6. F.P. 430606, 1911; abst. J.S.C.I. 1911, 30, 1375.

acid on cellulose or its derivatives in the presence of a small quantity of an aliphatic or aromatic ester of sulfuric acid, as ethyl-sulfuric acid. Where the reaction is carried out in the absence of solvents, gelatinous products are obtained, whereas viscous products result in the presence of solvents.

The Vereinigte Glanzstoff-Fabriken have shown[1] that the cellulose hydrates which may be obtained in large quantities at a low price in a form, for example, of denitrated nitrocellulose threads, lustracellulose filaments (cuprammonia process), or viscose, as refuse from the cellulose artificial silk industry, are highly adapted for serving as raw material for formylcellulose manufacture. They merely introduce the refuse material into ordinary formic acid of 95%-100% strength, warm the mass gently until the cellulose passes into solution, when the solution can be utilized directly by forcing through spinnerets into artificial filaments. The solution of the waste may be effected at the ordinary temperature, is accelerated by warming to 40°-50°, while at still higher temperature, although solution proceeds more rapidly, the solutions become thin, probably from further hydrolysis of the cellulose hydrates, and the formation of more highly and complexly hydrated formylcelluloses. The best criterion for the quality of the product which it is desired to obtain is the gloss and elasticity of the film prepared from the solutions.[2]

1. U.S.P. 1046729, 1912; 1055513. 1913; abst. Mon. Sci. 1913, **78**, 151; C.A. 1913, **7**, 700, 1608. E.P. 15700, 1910; E.P. 6241, 1911, being addition to E.P. 15700, 1910; F.P. 420856, 1910; First Addition thereto dated Mar. 13, 1911; D.R.P. 233589, 1909; abst. Wagn. Jahr. 1911, II, 421. D.R. Anm. B-69304; V-8974; V-9653; abst. Kunst. 1913, **3**, 479. Belg. P. 234433, 1911; Aust. P. A.-5148, 1910; Swiss P. 53585, 1910; Hung. Anm. G.-3306, 1911; abst. J.S.C.I. 1910, **29**, 1199; 1911, **30**, 279, 1050; 1912, **31**, 279.

2. It is claimed to be preferable not to attempt to produce a solution of greater concentration than 6% and at a temperature of about 25°. From this, excess of formic acid may be distilled off in a partial vacuum, until the desired consistency is obtained. This method permits not only the economical recovery of much of the excess of formic acid employed, but also facilitates the incorporation with the formylcellulose of any other materials which are soluble in formic acid, such as plastic-inducing bodies.

Not only is artificial filament waste utilizable, but solutions of cellulose which for any reason are defective for spinning purposes may be precipitated in bulk, the cellulose recovered, purified and converted into formate. If the case should arise of a shortage of such artificial filaments, they may be produced intentionally by dis-

If desired, the cellulose may be dyed before formylation, thus producing various shades, for the dyestuffs used—algol, indanthrene, rosanthrene, helindon, katigen, immedial, etc.—are stable against the acid agents employed in the formylating process.[1] For example, 200 parts of cotton dyed with indanthrene RS are formylized with 100 parts formic acid, and 3-10 parts sulfuric acid, a dark blue solution being obtained from which the deep blue formylcellulose can be precipitated and washed in the usual manner with water without detriment to the color. It is soluble in the usual solvents, and the blue films may be produced from the solutions. The process is carried out in an analogous manner by using other suitable dyestuffs.

G. Bonwitt has described[2] the preparation of artificial products from viscose and the cellulose formates as carried out in Germany at the present time, in which cellulose xanthogenate resulting from the action of carbon bisulphide on alkali-cellulose is left to mature at rest for one or two days, the granular mass being worked up for about an hour in a kneading machine and allowed to remain another 24 hours at rest. The homogeneous paste is forced through a cording press to eliminate air bubbles and is then charged direct into pipes or receivers in which it is dried for 24-36 hours at a temperature of 30°. During this treatment the cellulose xanthogenate is decomposed and cellulose is produced. The heating is performed in closed vessels to prevent frothing by

solving cellulose in cuprammonia, precipitating with acid or alkali without the formation of threads, freed from copper, washed and dried. This amorphous cellulose hydrate, corresponding to the artificial silk refuse, which has passed through the entire process of spinning and shaping, is said to be different from that obtained for example, by soaking 1 molecule of cellulose in one-half molecule of copper in the form of cuproammonia, or by the alkaline hydroxide mercerization of cotton. The purposely produced amorphous hydrate, the patentees state, forms esters somewhat more slowly than the regular thread waste, and yields comparatively thick solutions, undoubtedly because the cellulose aggregate is more highly or differently hydrated than the perhaps more uniformly dried threads.

1. U.S.P. 994738, 1911; E.P. 1556, 1911; F.P. 427425, 1911; D.R.P. 237210, 1910; Belg. P. 233786, 1911; Aust. Anm. A.-2376, 1911; abst. J.S.C.I. 1911, **30**, 888, 1051, 1236, 1309; Chem Ztg. 1912, **36**, 252.

2. U.S.P. 804960, 1905; E.P. 6751, 1905; F.P. 352897, 1905; D.R.P. 175379, 1904; 188542, 1905.

the evolution of carbon bisulfide and deformation of the mass. The solids so produced next undergo lixiviation by a special process and then consist of pure cellulose of rubber-like consistence. The products are dried in vacuum chambers with special precautions to prevent deformation, which very readily occurs with uneven drying. All kinds of inert and colouring matters suitable for particular purposes may be incorporated with the viscose paste. The moulded masses may be polished by dipping them in a 10 per cent. solution of viscose and fixing the film by heating at 100°, and they may be waterproofed by similar treatment with a solution of nitro-cellulose or cellulose acetate. Films, dialysers and solid articles are also produced from formylcellulose. The only factory at which this process is worked is at Sydowsaue, and the raw material is hydrated cellulose in the form of artificial silk waste. This is readily dissolved by 90-95 per cent. formic acid yielding pure cellulose triformate. The product of the reaction is dissolved in hot lactic acid and, after distilling off the formic acid, a clear ropy syrup is obtained which solidifies on exposure to the air to a plastic solid. According to another process which is also worked, the solution of cellulose formate is precipitated by amyl acetate, amyl formate or alcohol or a mixture of a hydrocarbon and alcohol. A tough plastic mass is thereby deposited which may be worked up in the usual way with camphor or camphor substitutes.

The solvents of cellulose formate are limited, many of the cellulose acetate solvents such as acetylenetetrachloride alone, or with methyl alcohol,[1] triphenyl phosphate,[2] benzyl benzoate,[3] methyl formate,[4] chloroform, acetone, chloral,[5]

1. U.S.P. 1009116, 1911; F. P. 417319, 1910.
2. E.P. 10794, 1910; F.P. 415517, 1910, without urea. E.P. 10795, 1910; F.P. 415518, 1910, with urea.
3. U.S.P. 1027619, 1912; F.P. 432264, First Add. thereto dated July 7, 1911; Second Add. thereto, dated July 15, 1911; Third Add. thereto, dated Sept. 13, 1911; E.P. 20978, 1911; Belg. P. 241250. See also U.S.P. 961360, 1910; E.P. 13692, 1910.
4. U.S.P. 972464, 1910.
5. E.P. 9357, 1907; F.P. 377010, 1907; D.R.P. 189703, 1902, Addition to D.R.P. 152111, 1902; D.R.P. 220228, 1907. F.P. 432264, 1911; Belg. P. 241251, 1911. Add. 16854 to F.P. 432264; abst. Kunst. 1913, 8, 258, combines phenolates or alcoholates with chlorine derivatives of ethylene or acetylene. U. S. P.

chloranisol,[1] chlorhydrins,[2] chlorobenzylic alcohol,[3] creosote,[4] diaceton alcohol,[5] epichlorhydrin,[6] acetin,[7] methyl formate, mannol,[8] naphthyl acetate,[9] nitrobenzene,[10] nitromethane,[11] pentachlorethane and alcohol,[12] benzyldihydropulegone,[13] chloral alcoholate,[14] acetyl alkyl aniline,[15] naphthol acetate,[16] chlorpalmitic acid,[17] ethylenechlorhydrin,[18] acetodichlorhydrin and alcohol,[1] ethylene chloride and alcohol,[2]

774677, 1904; E.P. 7088, 1902; F.P. 319724, 1902; Addition No. 811, dated Mar. 18, 1902, to F.P. 319724; D.R.P. 145106, 1902; D.R.P. 151918, 1902, Addition to D.R.P. 145106; D.R.P. 152111, 1902. E.P. 27258, 1910; F.P. 419530, 1910; Addition No. 13237, dated Sept. 29, 1911, to F.P. 419530. E.P. 11354, 18193, 1909; E.P. 13100, 1910; F.P. 408370, 1910; First Add. No. 12469, dated April 13, 1910, to F.P. 408370; Second Addition dated Jan. 11, 1910; Aust. Anm. 29b, 1642, June 21, 1909. The Internationale Celluloseester Ges. (D.R.P. 265911, 1913; abst. C.A. 1914, 8, 573) employ as solvents in the manufacture of cellulose formate solutions of chloral hydrate and chloral alcoholate.

1. F.P. 432264, 1911; Belg. P. 241251, 1911.

2. U.S.P. 1005454, 1911; E.P. 476, 1910; F.P. 411298, 1910; Aust. P. 50656, 1910; Belg. P. 222106, 1910; Hung. Anm. M.-3691, Dec. 30, 1909; Swiss P. 51839, 1910.

3. F.P. 432264, 1911; Belg. P. 241251, 1911.

4. F.P. 354942, 1905; First Addition thereto dated June 8, 1905; E.P. 12277, 12278, 1905; D.R.P. 185240, 185241, 1906. E.P. 12976, 1909; F.P. 411126, 1909; Aust Anm. 9533, June 2, 1909; Hung. Anm. R.-2398, Dec. 23, 1909; Port. P. 7102, Dec. 12, 1909.

5. U.S.P. 1003438, 1911; E.P. 11728, 1911; F.P. 429754, 1911; D.R.P. 246967, 1910; Can. P. 136538, 1911.

6. U.S.P. 734123, 1903; 790565, 905; E.P. 21628, 1901; D.R.P. 153350, 159524, 1901; F.P. 317007, 1901; It. P. 62042, 1901; Aust. P. 31391.

7. F.P. 397429, 1908; D.R.P. 228867, 1907; F.P. 417027, 1910; E.P. 19735, 1908; F.P. 393963, 1908; D.R.P. 223793, 1907; Aust P. 51094, 1908; D.R.P. 210519, 1907; U.S.P. 1015155, 1912; Swiss P. 52437; Aust. P. 47889.

8. F.P. 432264, 1911; Belg. P. 241251, 1911.

9. U.S.P. 729990, 1903; D.R.P. 162239, 1902.

10. U.S.P. 734123, 1903; 790565, 1905; E.P. 21628, 1901; D.R.P. 153350, 159524, 1901; F.P. 317007, 1901; It. P. 62042, 1901; Aust. P. 31391.

11. D.R.P. 201907, 1907.

12. F.P. 432047, 1911; abst. Mon. Sci. 1913, 78, 40. Belg. P. 241252, 1911; F.P. 432264, 1911; Belg. P. 241251, 1911.

E. P. 2511, 1907; F.P. 276262, 1907; D.R.P. 189836, 189837, 1908; abst. J.C.S. 1908, 94, 1, 321; J.S.C.I. 1907, 26, 634, 988; Chem. Zentr. 1908. I. 320; C.A. 1907, 1, 2191, 1908, 2, 1508.

13. D.R.P. 202720, 1907.

14. E.P. 26657, 1909; F.P. 421010, 1910.

15. F.P. 427804, 1910.

16. F.P. 432264, 1911; Belg. P. 241251, 1911.

17. U.S.P. 855556, 1907; U.S.P. 962877, 1910.

18. U.S.P. 1027614, 1912. See also U.S.P. 1027617, 1912.

ethyleneacetochlorhydrin,[3] being unsuitable solvents or gelatinizing agents for the cellulose formates.

The Vereinigte Glanzstoff Fabriken A-G. have found lactic acid[4] to be an excellent solvent for the formates, Waite[5] having previously discovered the solvent action of this acid on the corresponding acetates. The Vereinigte dissolve 10 parts of artificial silk waste in about 100 parts of formic acid, then about 50 parts by weight of 80% lactic acid is added, and the excess of formic acid removed by distillation in a partial vacuum at a temperature of about 40°, and recovered for further use. The viscous syrup which remains may be drawn into threads, or allowed to solidify into a flexible and plastic mass. If it is desired to remove the acid reaction from the mass, dialysis with water is resorted to. Inasmuch as cellulose dissolves in formic acid to form a formylated derivative, it follows that the compound so formed is soluble in formic acid. The Internationale Zelluloseester-Gessellschaft[6] have patented a similar process in which formylated cellulose is made plastic by the combined action of formic and lactic acids. Instead of lactic acid use may be made of phosphoric acid, the commercial syrupy orthophosphoric acid having proved most suitable.[7] Best results are said to be obtained by mixing 1 kilo of approximately 99% formic acid with 1 kilo commercial phosphoric acid of about 84% strength, and 200 gm. of degreased, slightly bleached cotton stirred in. After remaining for a few hours the cellulose is converted into a slightly colored viscous solution, which can be worked into fibers, threads, etc. In

1. U.S.P. 1027486, 1912.
2. U.S.P. 1027616, 1912.
3. U.S.P. 1027615, 1912. See also U.S.P. 1027618, 1912.
4. E.P. 8313, 1911; F.P. 428069, 1911; abst. J.S.C.I. 1911, **30**, 1150, 1156.
5. U.S.P. 690211, 1901. See also Furst Guido Donnersmarck'sche Kunstseiden und Acetatwerke, D.R.P. 237599, 1907; U.S.P. 922340, 1909; E.P. 6554, 1909; F.P. 400652, 1909.
6. D.R.P. 239701, 1910. See also D.R.P. 151918, 189703, 220228.
7. E.P. 29246, 1910; E.P. 309, 1911; F.P. 423774, 1910; F.P. 424621, 1911; D.R. Anm. 39b, V.-9653, 1910; Aust. P. 39b, A.-9872, 1910; E.P. 3096, 1910; Swiss P. 53777; abst. J.S.C.I. 1911, **30**, 448, 615, 741, 888; C.A. 1911, **5**, 3340; Kunst. 1912, **2**, 255.

order to make this product plastic [1] a solution of this cellulose formate, or cellulose phospho-formate in formic acid, is diluted with amyl acetate, amyl formate, methyl alcohol, ethyl alcohol or a mixture of hydrocarbon and alcohol, the ester immediately separates as a coherent, viscous mass, which falls to the bottom of the vessel. The supernatant liquid may now be poured off, the precipitate washed with some precipitating agent, there finally remaining a semi-solid gelatinous coagulum, which is transparent, and readily miscible with triphenyl phosphate to a hard, solid, transparent and plastic mass.[2]

In a series of subsequent patents [3] have been described a number of substances suitable as cellulose formate solvents. Alkali iodides and bromides, calcium chloride, ammonium nitrate, alkaline-earth and metallic nitrates, cupric chloride, alkali xanthates, aniline salts and alkaline salts of aromatic mono- and poly-sulfonic acids are claimed as especially suitable. The solutions set to a jelly when cool, but become liquid again upon warming. The cellulose formate may be separated from these solutions in an unchanged form by means of suitable precipitants.[4] Soluble chromates and especially bichromates, give excellent permanent solutions. When 20 k. cellulose formate is dissolved in 30 k. ammonium bichromate in 100 l. of water and gentle heat applied, the formate passes into solution, forming a yellowish

1. U.S.P. 1029341, 1912; abst. J.S.C.I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164; E.P. 8313, 1911; abst. J.S.C.I. 1911, **30**, 1050; Chem. Tech .Rep. 1911, **35**, 556; 1912, **36**, 532; C.A. 1912, **6**, 3018. F.P. 428069, 1911; abst. J.S.C.I. 1911, **30**, 1156. Aust. Appl. 2994, 1911.

2. For instance, 1 kilo of artificial silk refuse is dissolved in 10 kilos 98% formic acid and mixed with 3-4 kilos amyl acetate. On stirring, a semi-solid mass of formylcellulose is thrown out, which upon standing automatically throws off further quantities of liquids, the contraction continuing until a jelly-like mass results. In this condition 2 kilos of camphor are added and the mass kneaded into a plastic. Or, 1 kilo of cotton or other cellulose may be stirred into a mixture of 10 kilos phosphoric acid of 1.75 sp. gr. and 10 kilos concentrated formic acid, and the ester precipitated by means of a mixture of toluol and ethyl alcohol. After the initially whitish coagulum has become nearly transparent and solid, 150 gms. triphenyl phosphate is incorporated.

3. D.R.P. 265852, 265911, 1913; 266600, 267577, 1913. D.R. Anm. V.-9693.

4. D.R.P. 266600, 1913; abst. J.S.C.I. 1914, **33**, 196; Kunst. 1913, **3**, 439; C.A. 1914, **8**, 573.

viscous liquid.[1] Solutions of mono- or poly-hydric phenols,[2] or chloral hydrate or a chloral alkyloxide (alcoholate)[3] may also be employed.

As far back as 1902[4] E. Thomson and J. Callan patented the use of cellulose esters, including the formate, as an insulating covering for electric conductors. The wire to be insulated is first given a coating of some adhesive as Canada balsam or Venice turpentine, after which the insulating solution of cellulose ester is applied in solution, several separate coats being required. C. Ellis[5] has described combinations of chloral with castor oil, amyl lactate, methyl acetone, methyl-ethyl ketone and cellulose formate as giving commercially valuable plastic bodies.

In the manufacture of artificial silk according to the process of the Chemische Fabrik von Heyden Aktiengesellschaft,[6] the formylated cellulose solutions are first diluted with a non-solvent nearly to the point of precipitation or coagulation so that when solutions are forced through capillary orifices into an aqueous precipitating bath, this penetrates at once, or at least more rapidly into the formed thread. As a result it is claimed the thread can be drawn off more rapidly with less danger of rupture, and subsequent sticking together of the formed filaments is obviated.

Judging by the great interest being displayed in this series of esters as exemplified by the references previously quoted, the majority of which represent work of the past five years or less, the cellulose formates before long will have established themselves on a firm economical basis as direct and satisfactory competitors with the analogous acetates. The discovery of suitable and inexpensive solvents and plastic-inducing bodies would be a long step toward placing this

1. D.R.P. 267557, 1913, being Add. to D.R.P. 266600; abst. J.S.C.I. 1914, **33**, 196; C.A. 1914, **8**, 822; Kunst. 1913, **3**, 400.
2. D.R.P. 265852, 1913; abst. J.S.C.I. 1913, **32**, 1104; C.A. 1914, **8**, 573.
3. D.R.P. 265911, 1913; abst. J.S.C.I. 1913, **32**, 1104; Kunst. 1913, **3**, 474.
4. U.S.P. 695127, 1902; Reissue thereon 11997, 1902.
5. U.S.P. 999490, 1911; abst. J.S.C.I. 1911, **30**, 1051.
6. E.P. 3973, 1911; F.P. 426436, 1911; Aust. Anm. A.-327, 1911; abst. J.S.C.I. 1911, **30**, 950, 1156.

branch of the cellulose ester art on a firm basis.

According to the patented process of the J. P. Bemberg Aktiengesellschaft[1] gaseous hydrochloric acid is preferable because the process takes a more regular course and less secondary products are formed, the process being to introduce 2-4 parts dry HCl gas into 100 parts of formic acid of 98%-100% strength, after which 20-30 parts of dry cellulose is gradually added to the mixture. After several hours, assisted by repeated stirring, the cellulose passes substantially into solution, the temperature meanwhile being kept between 15°-18°. At the completion of the formylating process the mass is precipitated in a large bulk of water, washed until neutral and dried.

E. Worden[2] has endeavored to increase the number of suitable solvents for the cellulose formates by attempting partial hydration of formylated cellulose, in a manner similar to the well known process of George W. Miles, for the partial hydration of acetated cellulose. After formylation of the cellulose, selective hydration and partial saponification was attempted by means of the introduction of varying amounts of water for stated periods before the formylated mass was precipitated out, neutralized and dried. Progressive solubility experiments indicated that hydration did not increase the solubility to a commercially valuable degree.

Cellulose Propionates (Propionylcellulose). Many of the methods applicable for the preparation of the cellulose acetates are suitable for propionylcellulose formation. Among the earliest methods is that of C. Weber and C. Cross,[3] in which modified cellulose either in the form of cellulose hydrate or preferably that obtained from solutions of cellulose sulfocar-

1. E.P. 2511, 1907; F.P. 276262, 1907; D.R.P. 189836, 189837, 1908; abst. J.C.S. 1908, **94**, i, 321; J.C.S.I. 1907, **26**, 634, 988; Chem. Zentr. 1908, I, 320; C.A. 1907, **1**, 2191, 1908, **2**, 1508.

2. J.S.C.I. 1912, **31**, 1064-8. Reprinted Chem. Eng. 1913, **17**, 26. Reprinted Mon. Sci. 1913, **78**, [(5), 3], 388; abst. C.A. 1913, **7**, 888, 2304; Chem. Zentr. 1913, **84**, 1105; J.C.S. 1913, **104**, i, 19.

3. U.S.P. 632605, 1899. E.P. 22029, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 63101, 1899. D.R.P. 112817. Russ. P. 3264, 1900. Belg. P. 137577, 1898. Dan. P. 2558, 1899. Port. P. 2930, 1899. Belg. P. 137577 to Guido Henckel Donnersmarck covers the same ground, i. e., using nitrobenzene, epichlorhydrin or dichlorhydrin as solvents. Belg. P. 138462 is addition to it.

bonate, are heated with zinc or magnesium propionates in concentrated solution, propionyl chloride, and propionic anhydride. After heating the mixture on the water-bath until the mass thickens and substantially passes into solution, nitrobenzene is added in small quantities as a diluent to control the reaction and prevent the aggregation of the product into a solid mass. Epichlorhydrin or dichlorhydrin are other suitable diluents. The ester may be precipitated in fine flakes by pouring the solution into alcohol, filtered, washed free from acid and metallic propionate and dried. It is stated to retain its flocculent condition after drying and to be "soluble in any of the solvents for cellulose acetate."

According to Knoll and Co.[1] a mixture of 5 parts propionic anhydride with 5 parts of glacial acetic acid is made in which 0.2 part of ammonium sulfate is dissolved and to which 1 part of cellulose is added. The whole is heated up to not to exceed 70°, and after standing a short time the cellulose passes into a viscous solution of the propionate. In the C. Claessen method[2] cellulose may be converted into esters which are soluble in water, dilute alcohol, dilute acetone, and glycerol, but insoluble in pure alcohol or acetone, ether, and benzene, by treatment with anhydrides of fatty acids at temperatures of 70°-80°, in presence of acid sulfate of pyridine or its homologues, or quinoline sulfate. If the esterification is carried out in presence of a suitable solvent, such as glacial acetic acid, the ester is obtained in the form of a clear, viscous solution, from which it may be precipitated by means of alkalis or ammonia. For example, 2-5 gm. of cellulose, 15 gm. of glacial acetic acid, 12 gm. of propionic anhydride, and 4 gm. of acid pyridine sulfate are heated at 70° for four days; the

1. D.R.P. 203178, 1906; abst. Jahr. Chem. 1905-08, 984; Chem. Zentr. 1908, **79**, 1549; Chem. Zts. 1909, **8**, 1053; Mon. Sci. 1912, **77**, 97; Zts. ang. Chem. 1908, **21**, 2426; Wagn. Jahr. 1908, **54**, 366. D.R.P. 206950, 1907, being Addition to D.R.P. 203178; abst. Chem. Zts. 1909, **8**, 1183; Zts. ang. Chem. 1909, **22**, 656; Chem. Ind. 1909, **32**, 153; Wagn. Jahr. 1909, **55**, II, 397; Mon. Sci. 1912, **77**, 96. E.P. 2026-A, 1907; abst. J.S.C.I. 1908, **27**, 353.

2. D.R.P. 222450, 1908; abst. J.S.C.I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Chem. Zentr. 1910, 481; Wagn. Jahr. 1910, **56**, 434; Chem. Zentr. 1910, **81**, 48; Chem. Zts. 1910, **9**, 1902; C.A. 1910, **4**, 2875.

product is a clear, viscous mass. The aqueous solutions of this ester are liquid when warm, and gelatinize on cooling. Sulfates of aniline and bases other than pyridine also act as "contact substances," but do not give soluble esters.

Where hydrochloric acid is used as the esterizing body, concentrated hydrochloric acid corresponding to 0.1 part HCl is added to 5 parts propionic anhydride and 4-5 parts of glacial acetic acid, the addition of 1 part of cellulose causing solution as propionylcellulose to take place at about 70° in 12-24 hours.[1] Instead of free hydrochloric acid, the chloracetic acids have been found suitable in the hands of Actien- Gesellschaft fur Anilin-Fabrikation,[2] their preferred method being to dissolve 100 gms. of cellulose in 320 gms. monochloracetic acid, and 320 gms. propionic anhydride by the aid of the water bath at a temperature of 50°-52° until the reaction mixture becomes clear and homogeneous. The mass is then precipitated in a large bulk of water as white flocks, which when dried are soluble in such acetylcellulose solvents as ethylmethyl ketone, ethyl acetate and also in benzol, toluol, xylol and warm alcohol, from the latter solutions of which they gelatinize. L. Lederer first treats cotton[3] with an equal weight of acetic acid containing 2.5% of sulfuric acid, then with three times the weight of carbon tetrachloride is added, and the cellulose esterized with 4.5 times its weight of propionic anhydride which has been diluted with an equal weight

1. U.S.P. 891218, 1908; abst. J.S.C.I. 1908, **27**, 765; Mon. Sci. 1909, (4), **70**, 116. E.P. 2026-B, 1907; abst. J.S.C.I. 1908, **27**, 353. F.P. 373994, 1907; abst. J.S.C.I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 83; Chem. Tech. Rep. 1907, **31**, 302. D.R.P. 201233, 1906; abst. Chem. Zts. 1908, **7**, 993; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, 994; Chem. Ind. 1908, **31**, 587; Jahr. Chem. 1905-08, 982. D.R.P. 203178, 1906; abst. Chem. Zts. 1909, **8**, 1053; Zts. ang. Chem. 1908, **21**, 2426; Chem. Zentr. 1908, 1837; Jahr. Chem. 1905-08, 984; Chem. Ind. 1908, **31**, 741. Aust. P. 41831.

2. E.P. 14255, 1906; abst. J.S.C.I. 1907, **26**, 220; C.A. 1907, **1**, 1341. F.P. 368738, 1906; abst. J.S.C.I. 1907, **26**, 30. D.R.P. 198482, 1905; abst. Mon. Sci. 1911, (5), **74**, 54; Zts. ang. Chem. 1908, **21**, 1760; Chem. Zentr. 1908, 118; Jahr. Chem. 1905-08, II, 982; Chem. Ind. 1908, **31**, 378.

3. U.S.P. 999236, 1911; abst. J.S.C.I. 1911, **30**, 1050. E.P. 3103, 1907; abst. J.S.C.I. 1907, **26**, 889. F.P. 374370, 1907; abst. J.S.C.I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 84; Chem. Zts. 1907, **6**, 139.

of carbon tetrachloride. After the reaction is completed, the cellulose propionate, which is stated to still possess the structure of the original cotton, is washed to neutral reaction and dried at a low temperature. Of other methods of formation described, they are analogous to the preparation of the corresponding acetates.[1]

According to A. Stein[2] in the case of hydrocellulose prepared by Girard's method, elementary analysis is not sufficiently accurate to determine the quantity of water chemically combined as the result of hydrolysis. Hydrocellulose esters of propionic, butyric and valeric acids have been prepared by the action of the acid anhydride upon Girard's hydrocellulose in presence of concentrated sulfuric acid. The products closely resembled cellulose acetates in their general properties; esterification proceeded easily until triacyl compounds were produced. This author has also prepared a series of acetic and butyric esters of hydrocellulose, using mono- and trichloracetic acids as catalysts. The products were for the most part soluble in chloroform, but contained small variable quantities of combined chlorine; the acetates thus obtained gave numbers considerably below those required by a cellulose triacetate, the highest product showing only 52.49% of combined acetic acid. A number of samples of commercial cellulose acetates were also analysed, two of which showed abnormally high values, 65.5% to 66.0% of combined acetic acid. These values would appear to confirm the view that hydroxyl groups are formed as the cellulose molecule is hydrolysed. For the analysis of cellulose acetates, the ester is treated with sulfuric acid, diluted with an equal volume of water, for two days and the acetic acid is distilled over at constant volume in a current of steam free from carbon dioxide. For the complete hydrolysis of the esters of higher

1. F.P. 430606, 1911; abst. J.S.C.I. 1911, **30**, 1375. F.P. 385179, 1907; abst. J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 106; Bull. Soc. Chim. 1909, (4), **6**, 557. F.P. 385180, 1907; abst. Mon. Sci. 1909, (4), **70**, 105; Bull. Soc. Chim. 1909, (4), **6**, 557. U.S.P. 695127, 1902; Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303.

2. Zts. ang. Chem. 1913, **26**, 673; abst. J.S.C.I. 1913, **32**, 1102.

homologues a stronger acid is required (1.8:1 for butyrates and 3:1 for valerates). The water in the steam generator should be boiled thoroughly and sodium hydroxide added; volatile acids are also produced at the expense of the hydrocellulose residue. To correct the results, distillation is carried on for a considerable time after the acetic acid has distilled over; at this stage the volatile acidity per 100 c.c. of distillate becomes practically constant. This constant is then applied as a correction for the volatile acidity of the volume of distillate obtained before constancy was reached. To avoid errors of titration, each increment of distillate should be added to the liquid which has already been titrated.

The experiments of R. Woodbridge[1] on the preparation of the tripropionate was confined to the action of an active dehydrating agent as zinc chloride or sulfuric acid upon filter paper and hydrocellulose prepared therefrom, in the presence of propionic anhydride or propionyl chloride. The product was completely soluble in chloroform and in ethyl acetate, his statement that solubility in ethyl acetate is a qualitative distinction from cellulose acetates being in error. On spontaneous evaporation of a chloroformic solution, the tripropionate films formed were not superior to those of the corresponding acetate, while the cost is considerably greater.[2] So far as the author is aware, the cellulose propionates, at the present time, have no industrial uses. Like the acetates, they are white amorphous powders, insoluble in water, benzine, benzene, toluene, xylene, amyl alcohol and acetate, soluble in acetone and the higher ketones, acetylene tetrachloride, pentachlorethane and alcohol, chloroform and ethyl acetate.

1. J.A.C.S. 1909, **31**, 1069; abst. Zts. ang. Chem. 1910, **23**, 144; J.C.S. 1909, **96**, i, 768; J.S.C.I. 1909, **28**, 1061; C.A. 1910, **4**, 667; Chem. Zentr. 1909, 1216.

2. 2.5 gms. filter paper were treated with a mixture of 15 gms. propionic anhydride and 0.5 gms. sulfuric acid of sp. gr. 1.84, most of the cellulose dissolving after 41 hours. The mass was precipitated with water, washed, dried, and was found partially soluble in chloroform, apparently comprising unattacked cellulose and the tripropionate, saponification yielding 53.89% propionic acid, whereas a true tripropionate should yield 67.3%. For descriptive review of the propionates, including the esters, see A. Dubosc, Rev. gen. chim., 1910, **12**, 333.

Apparently no work has been done on the subject of partial hydration of the propionylcelluloses—a field which was so fruitful with the corresponding acetic esters.

Cellulose Butyrates at the present time have no commercial significance. Formerly they were advocated for many uses, but time has demonstrated that the less expensive acetates have more valuable properties. The butyric esters of cellulose have been claimed as especially applicable in the preparation of bronze paints and lacquers [1] in explosive manufacture,[2] for the insulation of wire,[3] the prepartion of storage battery plates,[4] and for waterproofing purposes,[5] especially in the treatment of starched linen.[6]

The butyrates may readily be prepared by the action of butyric acid, butyryl chloride and a condensing agent as zinc chloride,[7] ethylsulfuric acid [8] or sulfuric acid. In the patented method of C. Weber and C. Cross [9] 162 parts of cellulose, preferably that obtained from solutions of cellulose sulfocarbonate, are intimately mixed with a concentrated aqueous solution of 198 parts of magnesium butyrate and the mixture evaporated to dryness. To this mixture is then added 213

1. U.S.P. 884475, 1908; abst. J.S.C.I. 1908, **27**, 512. Can. P. 136538, 1911; abst. C.A. 1912, **6**, 303. E.P. 11728, 1911; abst. C.A. 1912, **6**, 3183.

2. E.P. 24662, 1898; abst. J.S.C.I. 1900, **19**, 375. For the sebacic esters of cellulose, see Knoll & Co., D.R.P. 203642, 1906; Zts. ang. Chem. 1908, **21**, 1760, 2334.

3. U.S.P. 695127, 1902; Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303.

4. U.S.P. 776192, 776480, 1904; abst. J.S.C.I. 1904, **23**, 1223. F.P. 375092, 1907; abst. J.S.C.I. 1907, **26**, 877.

5. U.S.P. 779553, 1905; abst. J.S.C.I. 1905, **24**, 139. D.R.P. 152630, 1904; Jahr. Chem. 1904, 239.

6. U.S.P. 1025731, 1912; abst. C.A. 1912, **6**, 1994. E.P. 12406, 1910; abst. J.S.C.I. 1911, **30**, 206. D.R.P. 242786, 1910; abst. C.A. 1912, **6**, 2182.

7. F.P. 385179, 1907; abst. Mon. Sci. 1909, (4), **70**, 105; Bull. Soc. Chim. 1909, (4), **6**, 557; J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383. F.P. 385180, 1907; abst. Mon. Sci. 1909, (4), **70**, 106; Bull. Soc. Chim. 1909, (4), **6**, 557; J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383.

8. F.P. 430606, 1911; abst. J.S.C.I. 1911, **30**, 1375.

9. U.S.P. 632605, 1899. E.P. 22029, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 63101, 1899. D.R.P. 112817; abst. Jahr. Chem. 1900, 843; Wagn. Jahr. 1900, II, 450. Russ. P. 3264, 1900. Belg. P. 137577, 1898. Dan. P. 2558, 1899. Port. P. 2930, 1899; cf. D.R.P. 105347; Wagn. Jahr. 1899, 1064.

parts of butyryl chloride and about 25 parts of butyric anhydride. After standing for some time the temperature rises and the mixture begins to thicken. A diluent as nitrobenzene is then gradually added, the total quantity employed depending upon the fluidity of the final product desired. A mixed butyro-acetate or aceto-butyrate of cellulose is said to result if the magnesium butyrate is treated with acetyl chloride. Treatment of 157 parts of acetyl chloride with 25 parts of butyric anhydride yields a cellulose aceto-butyrate, of no particular value over the simple acetate. It is claimed by the patentees that the method is applicable to the preparation of higher cellulose esters as cellulose heptylate, oenanthate, caproate, caprate, stearate, angelate, hexanoate, hybogaete, and oleate; also aromatically substituted esters such as cellulose phenyl-acetate and phenyl-propionate. If their preparation is possible, they are of no present technical value.

L. Lederer[1] first hydrolyzes the cotton with an equal weight of glacial acetic acid containing 2.5% of sulfuric acid, then three times the weight of carbon tetrachloride is added and the cellulose acetylized with 5.6 parts of butyric anhydride which has been diluted with an equal volume of carbon tetrachloride. The acetylized cellulose is then centrifugalized, washed to neutrality and dried.

Cellulose angelate,[2] benzo-acetate,[3] phosphoacetate,[4] and sulfacetate[5] have been described, of indefinite composi-

1. U.S.P. 999236, 1911; abst. J.S.C.I. 1911, **30**, 1050. E.P. 3103, 1907; abst. J.S.C.I. 1907, **26**, 889. F.P. 374370, 1907; abst. J.S.C.I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 84; Chem. Zts. 1907, **6**, 139. For sebacic esters of hydrocellulose, see A. Stein, Dissertation, Dresden, 1911, p. 71.

2. U.S.P. 695127, 1902; Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303. Also U.S.P. 632605, 1899. E.P. 22029, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 63101, 1899. D.R.P. 112817. Russ. P. 3264, 1900. Belg. P. 137577, 1898. Dan. P. 2558, 1899. Port. P. 2930, 1899.

3. E.P. 22237, 1911; abst. J.S.C.I. 1912, **31**, 279. F.P. 435507, 1911; abst. J.S.C.I. 1912, **31**, 329. Belg. P. 239564, 1911.

4. E.P. 8646, 8647, 1910; abst. J.S.C.I. 1911, **30**, 533, 616; Chem. Tech. Rep. 1911, **35**, 307. F.P. 413657, 413658, 1910; abst. J.S.C.I. 1910, **29**, 1101. F.P. 414679, 414680, 1910; abst. J.S.C.I. 1910, **29**, 1199, 1228. Swiss P. 51644, 51910; abst. Kunst. 1912, **2**, 77, 99. Belg. P. 223996, 1910. Aust. P. 47244, 53109; abst. Kunst. 1912, **2**, 255.

5. E.P. 22237, 1911; abst. J.S.C.I. 1912, **31**, 279. F.P. 435507,

tion. The cellulose benzoates may be formed by the action of 2.4 parts of benzoic anhydride, 6 parts glacial acetic acid and 0.2 parts bromine upon cellulose or preferably hydrocellulose, the temperature of esterification being around 50°. In another method[1] by heating cellulose with benzoyl chloride to 150° with the addition of pyridine or nitrobenzene. The product of acetylation is precipitated by pouring into water. The cellulose benzoates have been patented as an air-repellant insulator[2] especially applicable in the coating of wire,[3] as an ingredient in explosives,[4] and when combined with chloral compounds as a useful thermoplastic material.[5]

Starch Formate. Formic acid swells starch in the cold, and if dry starch be mixed with 1.5-2 times its weight of 99% formic acid it disintegrates and swells to a paste inside of five minutes, which may be transformed into a clear, gummy mass by cautious heating on the water-bath. This solution when poured into a large volume of cold water, yields a heavy, flocculent precipitate, plastic at first, but changing upon washing with water to a granular mass, easy to filter. The product as prepared by Traquair[6] is a white powder, lacking the characteristic starch appearance, the yield being about 120%.[7] If starch is heated at 85° with twice its weight of substantially absolute formic acid for 30 hours, and the product precipitated from alcohol, washed and dried, analysis shows a fixation of

1911; abst. J.S.C.I. 1912, **31**, 329. Belg. P. 239564, 1911.

1. D.R.P. 139669; abst. Jahr. Chem. 1903, 1014; Chem. Ind. 1903, **26**, 167; Zts. ang. Chem. 1903, **16**, 285; Chem. Centr. 1903, I, 744. D.R.P. 243581, 1908; abst. J.S.C.I. 1912, **31**, 381; C.A. 1912, **6**, 2316. E.P. 2527, 1912.

2. F.P. 375092, 1907; abst. J.S.C.I. 1907, **26**, 877.

3. U.S.P. 695127, 1902; Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303.

4. E.P. 24662, 1898; abst. J.S.C.I. 1900, **19**, 375.

5. U.S.P. 999490, 1911; abst. J.S.C.I. 1911, **30**, 1051.

6. J.S.C.I. 1909, **28**, 290; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1152-53.

7. If the clear gummy solution is diluted with an equal volume of 90% formic acid instead of water, and heated for a few minutes before pouring into water, the product retains its plasticity, can be drawn into fine threads and dries to a clear gum-like mass. It, however, is unstable in the air. According to U.S.P. 778173, 1904; E.P. 9868, 1902, starch formate may be prepared by mixing dry starch in a cylindrical vessel with 10% of its weight of formic acid introduced in the form of a spray, the mixture being heated at a

55% of formic acid, which corresponds nearest to a tri-formate on a C_6 molecule. The product gives no blue color with iodine upon saponification, indicating the product to be a derivative of starch resolution bodies, such as dextrin.

In the technical production of starch formate, many difficulties have arisen. Formic acid cannot be directly sprayed upon the starch due to its property of swelling the starch granule, the aqueous formic acid not allowing of uniform and satisfactory conversion. Formic acid solutions of 40% and over swell starch in the cold, weaker solutions inducing hydrolysis rather than formylation. It has been found, however, that a mixture of ordinary methylated spirits or suitably denatured ethyl alcohol with 90% formic acid does not swell to an injurious extent the starch granule, the lowest effective proportion of spirits being one part to two of formic acid. The time of conversion, however, has to be carefully limited in order not to produce water-soluble modifications, which, being washed away during the neutralization of unchanged formic acid, seriously decreases the yield. Starch formate is prone to decomposition by elimination of formic acid, and this tendency to the production of an acid reaction upon standing has been a serious difficulty in the way of its technical utilization, as in the majority of industries where it would otherwise be applicable, the product is precluded on account of proneness to develop an acid reaction by HOH hydrolysis.

Starch Acetate [1] was first prepared by P. Schuetzenberger in 1870,[2] who observed that the facility with which acetic anhydride attacks starch varies greatly with the state of aggregation of the starch granule and with the purity of the

low temperature for several hours with continual agitation, until a product of the required degree of formylation is obtained. The cooled product is either washed with water to remove the free formic acid, or the acid left in the starch may be neutralized by the addition of borax or an alkaline carbonate.

1. For resume of starch acetates patent and literature references, see E. C. Worden, Kunst. 1913, **3**, 61-3; abst. C.A. 1913, **7**, 1633.

2. Ann. Chim. Phys. 1870, (4), **21**, 235-264; abst. Chem. Centr. 1871, (3), **2**, 568; Reproduced in Ann. Chem. Pharm. 1871, **160**, 74-100; abst. Chem. Centr. 1871, (3), **2**, 740; Jour. Chem. Soc. 1872, **25**, 66.

3. Where starch was treated with 2.5-3 volumes of anhydride

anhydride.[2] Upon heating a mixture of starch and acetic anhydride to 150° the mass swelled, then dissolved into an amber-colored syrup, from which by addition of water an abundant flocculent white precipitate was formed, insoluble in water, alcohol or ether, but readily dissolving in glacial acetic acid. It rotated the plane of polarization strongly to the right.[1]

In Watt's Dictionary of Chemistry, 1877, 5, 410, line 2, appears the statement that glacial acetic acid in a sealed tube with starch converts it into "soluble starch," but no authority for the statement is given. L. Schulze in 1883[3] recorded his experiments upon the action of dilute acetic acid upon starch, in which best results were obtained with rice starch in a 10% solution when heated for four hours under pressure with 20% acetic acid. The starch is nearly all converted into dextrin, only traces of dextrose being formed. No products of acetylation are mentioned.

A. Michael[3] in endeavoring to ascertain whether the typical physical differences of potato and corn starch could be determined in their acetyl derivatives, acetylated them with acetic anhydride and acetyl chloride, and studied the properties of the esters thus formed. He found the acetated granules under the microscope could not be distinguished from those of the parent starches, and are not colored by iodine. His results led to no conclusion as to chemical differences in the properties of the two acetylated starches.[4]

and the latter contained 10-15% acetic acid, the starch was observed to swell greatly and to only partially pass into solution, although when precipitated with water it gave a voluminous white precipitate insoluble in alcohol, ether or glacial acetic acid, gave no blue color with iodine, and was readily saponified with alkalis. Although the amount of anhydride and length of time and temperature of acetation was varied, no higher derivative than the triacetate on a C_6 formula could be obtained.

1. With a 9.1% concentration in acetic acid in a 100 mm. tube, the deviation with gas illumination was 11°, corresponding to (a) = 120.8°.

2. J. prakt. Chem. 1883, **136**, 324; abst. Chem. Centr. 1884, (3), **15**, 217; Jahr. Chem. 1883, 1366; Jour. Chem. Soc. 1884, **46**, 284; Bull. Soc. Chim. 1884, **42**, II, 292.

3. Am. Chem. Jour. 1883-1884, **5**, 359-360; abst. J.C.S. 1884, **46**, 420; Bull. Soc. Chim. 1884, **42**, II, 354; Jahr. Chem. 1883, 1366.

4. Two grams of corn (maize) starch were heated with 5 gms. of acetyl chloride for 15 hours at 55-58°, the product was extracted

According to Z. Skraup and H. Hamburger[1] starch gives by weak acetylation an acetyl derivative which upon alkaline saponification yields a product having the essential properties of soluble starch in that it is colored blue with iodine and does not reduce alkaline cupric tartrate solution. Upon more energetic acetylization a substance is obtained which reduces copper solution and is no more colored with iodine. It would therefore appear that by energetic acetylation a transformation takes place similar in many respects to that observed in hydrolytic processes, only this transformation takes place with the addition of acetic anhydride.[2]

D. Law[3] in investigating the action of an acetylizing agent recommended by Cross, Bevan and Briggs[4] and obtained by adding 100 grams acetic anhydride to a solution of 50 grams of zinc chloride in 100 grams of glacial acetic acid, found that, although with cellulose a triacetate is given, with starch it does not react at all.[5] It gives a triacetate, with dextrose a tetra-acetate, and with sucrose an octa-acetate; with starch it does not react at all.[6]

with chloroform, the solution evaporated to dryness, the residue being dissolved in hot alcohol and clarified by filtration through bone-black. On cooling a greyish-white substance separated, from which, by again dissolving in hot alcohol and cooling, deposited a white amorphous substance, which softened at 148° and melted constantly at 151-152°. On the addition of water to the alcoholic filtrate, it gave a substance melting at 128-129°.

1. Ber. 1899, **32**, 2413-14; abst. J.S.C.I. 1899, **18**, 941; Chem. Centr. 1899, II, 752; Jahr. Chem. 1899, 1288; J.C.S. 1899, **76**, 852.

2. This is demonstrated by the behavior of cane sugar, when the latter is acetylated by acetic anhydride and sulfuric acid. In this reaction acetyl-saccharose is not obtained, but considerable quantities of penta-acetylglucose m. pt. 113°, accompanied by non-crystallizable bodies.

3. Chem. Ztg. 1908, **32**, 365-366; abst. J.C.S. 1908, **94**, 321; Bull. Soc. Chim. 1909, (4), **6**, 157; Zts. ang. Chem. 1908, **21**, 1377; Chem. Zentr. 1908, I, 183, Jahr. Chem. 1905-08, II, 55.

4. Jour. Soc. Dyers Col. 1907, **23**, 250. See also C. Cross and E. Bevan, Chem. Ztg. 1905, **29**, 527; Wagn. Jahr. 1905, II, 197; Chem. News, **41**, 304.

5. This is at variance with the author's experience, who has acetylated starch with substantially the above formula, the ratio of dry starch to anhydride being one to four.

6. Skraup and his co-workers (E. Geinsperger, E. von Kraffl-Lenz, F. Menter and H. Sirk) (Monats. 1905, **26**, 1415-72; abst. J.C.S. 1906, **90**, 67; Jahr. Chem. 1905-08, II, 929; Chem. Centr. 1906, II, 655) found that when soluble starch was suspended in eight times its weight of acetic anhydride saturated with hydrogen

F. Pregl [1] instead of acetylating ordinary starch, used the soluble starch prepared by the method of K. Zulkowsky,[2] but using 100 grams potato starch per kilo of glycerol. Upon acetylation by acetic anhydride in the presence of a small quantity of sulfuric acid in the cold, an amorphous triacetyl derivative is formed, which did not reduce copper or bismuth salts and was not colored by iodine.[3] Acetylation with an increased amount of sulfuric acid yielded a product having the empirical formula $C_6H_7O_5(CH_3COO)_3$, which was soluble in alcohol and reduces alkaline copper solutions. Hydrolysis yielded a dextrin which gave a red coloration with iodine and could not be identified with any dextrin previously described.[4]

chloride at -20°, the chief product after 14 days standing at the laboratory temperature was chlorononadeca-acetylerythrodextrin, while after two months an amorphous substance having the composition of acetylchloromaltose resulted. After four months, tetra-acetylchlorodextrose.

Chlorononadeca-acetylerthrodextrin $(C_6H_7O_5)Cl(CH_3COO)_{19}$, is soluble in benzene, insoluble in light petroleum, and when treated with silver acetate in glacial acetic acid solution, yields the icosa-acetyl derivative $(C_6H_7O_5)_3(C_6H_7O_6)(CH_3COO)_2O$, which sinters at 110°, and when hydrolyzed by means of 2N alcoholic potassium hydroxide yields erythrodextrin. The product obtained by shaking soluble starch with acetic anhydride saturated with hydrogen chloride at 0° for seven hours in a sealed tube at 40° is a mixture of acetyl-chloro derivatives of the starch and its decomposition products. When heated on the water bath with silver acetate in glacial acetic acid the acetochloro derivative of soluble starch yields Pregl's triacetyl soluble starch (Monats. 1901, **22**, 1049-1066; abst. J.C.S. 1902, **82**, 135-136; Chem. Centr. 1902, (5), **6**, 182, and a substance containing the acetyl derivatives of the decomposition products of soluble starch, as on hydrolysis it yields a substance giving a violet coloration with iodine.

1. Wien. Akad. Ber. 1901, **110**, IIb, 881-898; Monats. 1901, **22**, 1049-1066; abst. J.C.S. 1902, **82**, 135-136; J.S.C.I. 1902, **21**, 129; Bull. Soc. Chim. 1902, (3), **28**, 929; Chem. Centr. 1902, I, 182; Jahr. Chem. 1901, 880.

2. Ber. 1880, **13**, 1395-98; Wien. Akad. Ber. 1880, **72**, II, 384; abst. J.C.S. 1880, **38**, 865; Chem. Centr. 1880, (3), II, 613-14; Jahr. Chem. 1880, 1005. His method is to heat potato starch with glycerol at 180-190° for half an hour, or if rice or wheat starch is used, the conversion takes place more slowly. The solution is allowed to cool to 120°, when it is poured into three times its volume of strong alcohol. The precipitated starch is washed with alcohol until free from glycerol. It may be further purified by solution in warm water and precipitation by alcohol. The concentrated aqueous solution slowly deposits insoluble starch, while dilute solutions are precipitated by lime and baryta water and are colored blue by iodine.

3. It sintered at 260°, decomposed at 275°, and had $(a)_D$ + 191.73° at 20°. Molecular weight determinations showed, however, that the molecular weight must be from eight to nine times that

Instead of acetic anhydride saturated with hydrogen chloride, Kldiaschwili[1] employs dichloracetic acid, his preferred method being to heat 1 part of rice starch with 2 parts by weight of dichloracetic acid under a reflux condenser until the color reaction with iodine can no longer be observed. The product is then precipitated in water and dried over sulfuric acid.[2]

Cross, Bevan and Traquair[3] found that the extent of the

corresponding with the empirical formula. The product obtained by hydrolysis of the acetyl derivative was identical with the soluble starch and had $(a)_D$ +191.73° at 20°, soluble starch giving +191.27° at 20°. Both gave the formula $C_6H_{10}O_5$. V. Syniewski (Ber. 1898, **31**, 1791-1796; abst. J.C.S. 1898, **74**, 551; J.S.C.I. 1897, **16**, 1029), acetylated soluble starch, and obtained the derivative $C_{16}H_{20}O_9(CH_3CO)_7$ by heating soluble starch with barium carbonate and acetyl chloride in sealed tubes at 120° and afterwards at 140°, the product obtained being a white amorphous powder melting at 110-112°. The corresponding benzoyl derivative $C_{16}H_{20}O_9(C_6H_5CO)_7$ melts above 120°.

4. The following method gives the compound insoluble in alcohol: 5 grms. of soluble starch are shaken with 4 cc. acetic anhydride and 2.5 cc. strong sulfuric acid, the starch gradually dissolving upon shaking. After 48 hours the solution is poured into much water, the product well mixed and ground with water, filtered, washed and dried in vacuo over sulfuric acid, the yield being 132% of the starch. It was found free from ash and sulfur. Molecular weight determinations which were not concordant, showed that the molecule of the acetyl compound must be 8 or 9 times that of the empirical formula.

The acetyl derivative soluble in alcohol is obtained by mixing 5 gms. of starch in fine powder and vacuum dried, with 25 cc. acetic anhydride and then with a freshly prepared, somewhat cooled mixture of 3 cc. anhydride and 2 cc. strong sulfuric acid. When the temperature has fallen to 70-80° the solution is poured into water, the product obtained well washed and air dried. Yield 140%. The product is then dissolved in its volume of alcohol on the water bath, the solution cooled and the deposit then redissolved and again precipitated three times, after which it is allowed to slowly (one drop in two seconds) fall through a column of ether 90 cm. long. The acetyl compound thus obtained has the rotation $(a)_D$=187°, is very soluble in water, the solution giving a red coloration with iodine, while the acetate gave no reaction. The substance deports itself like an erythrodextrin. It reduces Fehling's solution, the reduction being about 12.5% that of glucose.

1. J. Russ. Phys. Chem. Soc. 1905, **37**, 421-23; abst. Brewers' Jour. 1905, **41**, 688; J.S.C.I. 1905, **24**, 1246; Jahr. Chem. 1905-08, II, 954; Chem. Centr. 1905, II, 1029.

2. Molecular weight determinations in acetone solution of the dextrin dichloracetic ester thus obtained indicated a sextuple molecule. The proportion of dextrin in the ester was determined by saponification by calcium hydroxide and precipitation of the dextrin by alcohol.

3. Chem. Ztg. 1905, **29**, 527; abst. Chem. Centr. 1904, II, 36;

action of glacial acetic acid on starch at 100-105° is proportional to the time of heating and to the ratio between acid and carbohydrate. The acetyl compounds formed during the earlier stages of acetation are insoluble in water, while those formed in the later stages are soluble. They found the action of glacial acetic acid on cellulose to be similar to that on starch.

Traquair found [1] that acetic anhydride alone has no action upon starch, even after two days, while at the boiling temperature (about 140°) but little acetylation occurs, after eight hours' treatment but 2.5% acetic acid having combined with the starch. This is significant in comparison with the fact that starch when treated with glacial acetic acid at 120° shows acetylation to a greater extent, eight hours' treatment giving a product containing 16% acetic acid, which is equivalent to a mono-acetate on a C_{12} formula. Prolonged treatment of starch with five times its weight of acetic anhydride at 90° gave the following results:

Time of Treatment	Acetic acid by saponification Per cent. in dry product
15 hours	12.1
24 hours	26.2
40 hours	38.5
74 hours	46.8

The products obtained are all insoluble in water, and readily saponified by alkalis with regeneration of the starch. The starch granules suffered little alteration, even after 74 hours. Starch acetates produced from glacial acetic acid are soluble often in cold water, which distinguishes them from the corresponding products obtained from acetic anhydride, and is undoubtedly due to the hydrolyzing action of the small percentage of water contained in the dry starch and glacial acetic acid. Acetic anhydride would combine with that water to the formation of acetic acid. As in the production of the corresponding nitric esters, by variation of the proportion of acid and the length of time and temperature of the acetation process an indefinite number of intermediate products may be obtained

Jahr. Chem. 1905-08, II, 948; Jour. Soc. Dyers and Col. 1905, 21, 192.

1. J.S.C.I. 1909, 28, 288; abst. Zts. ang. Chem. 1909, 22, 2346; Bull. Soc. Chim. 1909, (4), 6, 1152-53; Chem. Zentr. 1909, I, 1989; Jahr. Chem. 1909, 378.

which may be most readily distinguished by variation in their solubility.

W. Oechner de Conick and A. Raynaud [1] have studied the action of formic and acetic acids on starch and dextrin, and find that whereas when equal quantities of starch or dextrin are heated with increasing quantities of hydrochloric or hydrobromic acids for the same length of time, the degree of hydrolysis is proportional to the concentration of acid employed, but the quantity of dextrin hydrolyzed is always in excess of the quantity of hydrolyzed starch. With acetic acid and formic acid as hydrolytic agents, however, the reverse is the case, for, although the amount of hydrolysis is still proportional to the concentration, the quantity of dextrin and starch hydrolyzed are substantially the same, thus establishing a marked difference in hydrolysis between mineral and organic acids.

Cellulose Aceto-Nitrates. Chemical combinations of cellulose with acetic and nitric acid radicals have been described by C. Haeussermann,[2] L. Lederer,[3] and E. Berl and W. Smith,[4] obtained either by acetylating nitrocellulose or replacing a

1. Bull. Acad. Roy, Belg. 1911, 213-15; 335; abst. J.C.S. 1911, **100**, 423; Chem. Zentr. 1911, II, 855; C.A. 1911, **5**, 2443. For the hydrolyzing action of formic acid on starch, see W. Oechsner de Conick, Bull. Acad. Roy. Belg. 1910, 515, 586; abst. C.A. 1911, **5**, 394; J.C.S. 1910, **98**, 654; Chem. Zentr. 1910, **81**, 1459. See also L. Schulze, J. prakt. Chem. 1883, **136**, N.F. **28**, 324; I. Frankhausen, Ding. Poly., **266**, 303. For the preparation of soluble starch by heating with dilute acetic acid, see E. Blumer, D.R.P. 137330, 1901; abst. Chem. Centr. 1901, I, 306; Jahr. Chem. 1903, 1005; Zts. ang. Chem. 1903, **16**, 90. F.P. 322206, 1902; abst. J.S.C.I. 1903, **22**, 310. E.P. 10872, 1902. Farbenfabriken vorm. F. Bayer & Co., D.R.P. 200145; abst. Jahr. Chem. 1905-08, II, 941.

2. Chem. Ztg. 1905, **29**, 667; abst. J.S.C.I. 1905, **24**, 748; Jahr. Chem. 1905-08, II, 983; Zts. ang. Chem. 1905, **18**, 1989; Chem. Centr. 1905, **76**, [(5), **9**], 760; J.C.S. 1905, **88**, 574; Wagn. Jahr. 1905, **51**, 192.

3. U.S.P. 1028748, 1912; abst. J.S.C.I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164. E.P. 19107, 1906; abst. J.S.C.I. 1907, **26**, 220. F.P. 368766, 1906; abst. J.S.C.I. 1907, **26**, 30. F.P. 402072, 1909; abst. Mon. Sci. 1911, (5), **74**, 153. D.R.P. 179947, 1905; abst. C.A. 1906, **1**, 1507; J.S.C.I. 1907, **26**, 889; Zts. ang. Chem. 1907, **20**, 1194; Mon. Sci. 1909, (4), **70**, 68; Jahr. Chem. 1905-08, II, 433; Chem. Zentr. 1907, **78**, 433; Wagn. Jahr. 1907, I, 419. D.R.P. 200149, 1905, being Addition to D.R.P. 179947; abst. Zts. ang. Chem. 1908, **21**, 2047; Wagn. Jahr. 1908 II, 365; Chem. Zentr. 1908, 557; Jahr. Chem. 1905-08, II, 986. D.R.P. 210778, 1906; abst. Chem. Zentr. 1909, 247; Chem. Zts. 1909, **8**, 1474; Zts. ang. Chem. 1909, **22**,

portion of the acetyl groups in cellulose acetate by the nitric acid radical. Haeussermann dissolves acetylhydrocellulose in 15 times its weight of fuming nitric acid, and after standing for some days pouring the clear viscous solution into water, whereby there separates out a white, voluminous amorphous powder, soluble in acetone, ethyl acetate and amyl acetate. This product is regarded as a nitrate of acetylated hydrocellulose in which nearly all the acetyl radicals are substituted by nitric acid.

Lederer has patented the idea of reducing the inflammability of nitrocellulose by partial replacement of nitro by acetyl groups. He treats nitrocellulose with acid chlorides and anhydrides, with or without the addition of a condensing agent. Suitable mixtures are said to be formed when 1 part of nitrocellulose, 2-3 parts of acetyl chloride or acetic anhydride, and 0.5 part of sulfuric acid is allowed to remain together for some hours at 20-30°, the product being purified by precipitation in water, washed to neutrality and dried. The mixed esters thus formed are soluble in acetone, burn much more quietly than the nitro-compounds, and can be partially or completely denitrated by treatment with suitable agents as the sulfides.[1] These esters are advocated as specially suitable

1620; Chem. Ind. 1909, **32**, 383; Jahr. Chem. 1909, 389; Wagn. Jahr. 1909, II, 390. E.P. 19107, 1906; F.P. 368766. D.R.P. 179947, cover the same ground, i. e., the treatment of nitrocellulose either with acetic anhydride or acetyl chloride, perhaps in the presence of carbon tetrachloride. D.R.P. 200149 adds treatment with glacial acetic acid, while U.S.P. 1028748; F.P. 402072; D.R.P. 210778, denitrates the mixed aceto-nitrate to decrease the inflammability.

4. Ber. 1907, **40**, 903; abst. J.S.C.I. 1907, **26**, 273; C.A. 1907, **1**, 2179; J.C.S. 1907, **92**, 289; Chem. Tech. Rep. 1907, **31**, 257; Jahr. Chem. 1905-08, II, 982; Zts. ang. Chem. 1908, **21**, 1185. See also Berl and Smith, J.S.C.I. 1908, **27**, 534; abst. Jahr. Chem. 1905-08, II, 985; Zts. ang. Chem. 1908, **21**, 2427. Ost, Zts. ang. Chem. 1906, **19**, 922. Green and Perkin, J.C.S. 1906, **89**, 811. Pictet and P. Genequand, Ber. 1902, **35**, 2526. Berl and Smith, Ber. 1908, **41**, 1837; abst. J.C.S. 1908, **94**, i, 505; Bull. Soc. Chim. 1909, (4), **6**, 499; Zts. ang. Chem. 1908, **21**, 1855, 2427.

1. The denitration of the acetyl-nitrocellulose may be effected by means of sulfides or hydro-sulfides or salts of the lower oxide of a metal which forms also higher oxides, preferably with the addition of a solvent of the ester, that the latter may be caused to swell and soften, such as alcohol or acetone. Cuprous chloride, or dilute soda solution are especially applicable, and facilitated by the presence of a softening substance to aid penetration of the filaments, fibers or bands.

for the manufacture of sheets, films, bands, and artificial silk.[1]

E. Berl and W. Smith found[2] that glacial acetic acid and acetic anhydride alone have no chemical action on nitrocellulose, a gelatinous solution being produced, from which, on pouring into cold water, unaltered nitrocellulose is reprecipitated. If, however, a small amount of a condensing agent as sulfuric acid be added to the gelatinous mixture, immediate and vigorous reaction occurs with partial replacement of the nitro groups by acetyl radicals. Upon the addition of water, a white, flocculent precipitate forms, which dries to a crumbly powder, soluble in chloroform and ether-alcohol, more so in acetone and ethyl acetate. Solutions of the latter leave on drying tough, somewhat flexible and transparent films, suitable for insulation purposes or artificial silk formation, inasmuch as they are but little more inflammable than acetylcellulose. The proportion of acetyl and nitro groups vary according to the time elapsing between the addition of the sulfuric acid and the pouring of the reaction mass into water.

Physical mixtures of cellulose nitrates and acetates have been patented by several inventors. J. Schmerber and L. Morane[3] describe an incombusible celluloid prepared by mixing the two esters by means of a solvent compatible to both as acetone or ethyl acetate. Their process may be carried out by adding a solution of 40-60 gm. of camphor in 50-60 gm. of methyl or ethyl alcohol to 100 gm. nitrocellulose and allowing the mixture to stand for 24-48 hours, after which is added 100 gm. acetylcellulose and 40-60 gm. acetone. A product very similar to celluloid is said to be formed in which the high inflammability is absent. Nitrobenzene may also be added in

1. Another example. 1 part of nitrocellulose is treated with a mixture of 41 parts nitric acid of sp. gr. 1.40, 25 parts sulfuric acid sp. gr. 1.83 and afterwards with 2 parts of acetic anhydride containing 0.5% sulfuric acid and 8 parts carbon tetrachloride. After the reaction has completed, the cellulose ester is washed free from acid by water or alcohol and dried at a low temperature. Instead of using sulfuric acid in the acetylating mixture, the patentee claims phosphoric acid, benzolsulfinic acid, or dimethyl sulfate as being equally efficient.

2. J.S.C.I. 1908, **27**, 538. Ber. 1907, **40**, 903; 1908, **41**, 1837. Jahr. Chem. 1905-08, 977, 983, 985.

3. E.P. 4863, 1903; abst. J.S.C.I. 1904, **23**, 382. F.P. 324121, 1902; abst. J.S.C.I. 1904, **23**, 569.

small amounts and is said to further reduce the speed of burning.

In the F. Meyer process [1] acetyl- and nitro-cellulose are simultaneously treated with a solvent and precipitant in order to produce masses which in a cold state are pasty, capable of being moulded and easily kneaded, and manipulated into various kinds of objects. According to their invention, the two esters, preferably in combination with camphor, acetin, naphthol or phenol ester, ethyl phthalate, are simultaneously treated with a solvent (chloroform, acetone, ethyl acetate, amyl acetate) and a non-solvent (water, benzene, petroleum, oil of turpentine) in such proportions that a gelatinous mass results, of suitable consistency to be worked on the rolls and to be shaped into the desired forms.

L. Lederer [2] forms artificial silk cheaper than acetate silk and less inflammable than nitrocellulose silk by mixing 6 parts of nitrocellulose, 2 parts triacetylcellulose, 27 parts acetone and 16 parts acetylene tetrachloride into a homogeneous solution, which, after filament formation and coagulation by alcohol, may be denitrated. The action of acetyl nitrate upon cellulose [3] has, as yet, not been recorded.

E. Zuehl [4] combines the well-known thermo-plasticity of a mixture of nitrocellulose and camphor with the uninflammability of cellulose acetate, and produces a new plastic of low flammability, incorporating camphor substitutes at the same time, if special properties are desired. According to D.

1. D.R.P. 210519, 1907; abst. J.S.C.I. 1909, **28**, 812; Zts. ang. Chem. 1909, **22**, 1620.

2. E.P. 11625, 1909; abst. J.S.C.I. 1909, **28**, 1030. F.P. 402072, 1909; abst. J.S.C.I. 1909, **28**, 1221. D.R.P. 240751, 1908; abst. C.A. 1912, **6**, 2179; Kunst. 1912, **2**, 15; Chem. Zentr. 1911, **81**, I, 1843; Zts. ang. Chem. 1912, **25**, 47; Chem. Ztg. 1911, **35**, 624; Chem. Ind. 1911, **34**, 793. D.R.P. 248559, 1909, being Addition to D.R.P. 240751, 1908; abst. Kunst. 1912, **2**, 296; Zts. ang. Chem. 1912, **25**, 1884; C.A. 1912, **6**, 2849; Chem. Tech. Rep. 1912, **36**, 437; Chem. Zentr. 1912, **83**, 305.

3. A. Pictet, D.R.P. 200201, 1907; abst. J.S.C.I. 1912, **31**, 958; Zts. ang. Chem. 1908, **21**, 2103; Chem. Zentr. 1908, II, 552; Jahr. Chem. 1905-08, 359; Chem. Tech. Rep. 1908, **32**, 434; Wagn. Jahr. 1908, II, 15.

4. U.S.P. 729990, 1903; abst. J.S.C.I. 1903, **22**, 817. D.R.P. 162239, 1902; abst. Zts. ang. Chem. 1906, **19**, 498; Chem. Centr. 1905, II, 1900.

Florentin,[1] useful mixed nitric and acetic esters may be produced by combining 10 gms. of cotton or normal or modified cellulose with a mixture of 30-40 parts of acetic anhydride, 40 parts glacial acetic acid and 2 parts of a mixture of 65 parts of nitric acid of 40°Be. and 35 parts of sulfuric acid of 66°Be. strength, the mixture being kept at a temperature of 45° until a product soluble in chloroform, formic acid, glacial acetic acid or tetrachlorethane is formed, when the ester is precipitated by water, benzene or carbon tetrachloride, and washed until all acid is removed. In another process,[2] cellulose derivatives containing small amounts of nitrogen, preferably in the form of the nitric ester, and insoluble in acetic acid and acetic anhydride, are treated with the usual organic esterifying mixtures in the presence of a catalytic agent. A cellulose nitrate of 1.5-3% nitrogen is prepared by treating cellulose with a mixture of nitric and sulfuric acids containing a large proportion of water (25-34%) for a period of from 10-20 hours. This product is acetylated by means of a mixture of 400 parts of glacial acetic acid, 200 parts acetic anhydride and 3 parts of sulfuric acid.

H. Nishida[3] has investigated three methods for the preparation of mixed acetonitric esters of cellulose. According to his experience the nitration of cellulose acetate by the action of nitric and sulfuric acids is difficult practically owing to the dense structure of the acetic ester, and the products are not homogeneous. The acetylation of nitrocellulose in the form of tissue paper by an acetylating mixture containing sulfuric acid is practicable, but entails a loss of reagents, the gelatinous product absorbing acetic anhydride which can only be removed by washing. Starting with a nitrated paper containing 12.42 per cent N., the author obtained a mixed ester,

1. F.P. 445798, 1912; abst. Kunst. 1913, **3**, 274; Mon. Sci. 1913, **78**, 143.

2. Aktien-Gesellschaft fur Anilin-Fabrikation, F.P. 449253, 1912; abst. Kunst. 1913, **3**, 196; J.S.C.I. 1913, **32**, 482; Mon. Sci. 1914, **80**, 5. E.P. 10706, 1912; abst. J.S.C.I. 1913, **32**, 597. In their E.P. 1156, 1914; Add. to E.P. 10706, 1912; abst. J.S.C.I. 1914, **33**, 688, cellulose derivatives made by the action of more or less concentrated nitric acid on cellulose, are treated by the usual methods of esterification for producing cellulose esters.

3. Kunst. 1914, **4**, 141; abst. J.S.C.I. 1914, **33**, 476; C.A. 1914, **8**, 2250.

with a yield of 169 per cent, showing on analysis 4.8 per cent N. and 29.7 per cent CH_3CO. The ester was only slightly inflammable. The best method for preparing these mixed esters was by simultaneous esterification by the "single bath" process. A whole series of esters of different compositions were obtained by varying the proportions of reacting acids. The most satisfactory product for celluloid manufacture was obtained with a mixture of concentrated sulfuric acid, 98 parts by vol.; nitric acid (1.5 sp. gr.), 52.5; acetic anhydride, 50. Six grms. of cotton wool were steeped in 300 c.c. of this mixture for 1 hour at 30°. The product, which was obtained with a yield of 167 per cent, contained 9.8 per cent N.; it was completely soluble in alcohol and camphor, was non-inflammable by heating and only ignited by direct contact with a flame. When converted alone, or in admixture with nitrocellulose, into a celluloid mass, it yielded products more stable and less inflammable than ordinary celluloid.

Cellulose Aceto-Sulphates. Cross, Bevan and Briggs[1] have described products formed by the action of acetic anhydride and glacial acetic acid upon cellulose in the presence of increasing proportions of sulfuric acid, a series of mixed aceto-sulfuric esters being obtained, containing proportions of combined sulfuric acid ranging from 5-25%. According to their observations, the formation of the members of this series takes place in a graduated manner, the particular equilibrium obtained being determined by the concentration of the sulfuric acid in the reacting mixture. The products may be approximately separated based upon their solubility in acetone.[2]

1. Ber. 1905, **38**, 1859; abst. J.S.C.I. 1905, **24**, 685; Jahr. Chem. 1905-08, II, 986; Bull. Soc. Chim. 1906, (3), **36**, 638; J.C.S. 1905, **88**, 512; Chem. Centr. 1905, **76**, 36; Wagn. Jahr. 1905, II, 399.

2. The most definite member of the series obtained contains 8.76% sulfuric acid in combination, yielding 50.6% acetic acid upon saponification. Insoluble in water, soluble in acetone and hot ethyl alcohol. the alcoholic solutions solidifying to a jelly upon cooling. It is distinguished by a relatively high (8%) hygroscopic moisture and by a capacity to absorb a large volume of water to form a voluminous coagulum or jelly. As the proportion of sulfuric acid is increased the products become entirely soluble in water, from which they may be precipitated by brine, in which stage they still preserve their colloid character as cellulose derivatives. Guido Henckel Donnersmarck has patented cellulose aceto-butyrate, aceto-propionate, phenyl-acetate and palmitate, which as yet have shown no commer-

In a subsequent communication [1] it would appear that the products formed were rather acetyl-cellulose sulfuric acids or acetyl-cellulose sulfonic acids. Hake and Lewis [2] have shown that when cellulose nitrates are treated with a sulfuric acid-containing acetylating mixture, a series of mixed esters are formed, containing both nitric, acetic and sulfuric acid groups, and analagous to the above bodies.

The Act.-Ges. fur Anilin-Fabrikation [3] prepare sulfonic esters of cellulose, by acting upon the aqueous sodium or potassium alkali solutions of cellulose by aryl sulfochlorides, usually at the ordinary temperature, and with or without the addition of benzol. The products obtained in general, are soluble in epichlorhydrin, chloroform and ethyl acetate.[4] No commercial interest at present attaches itself to these esters.

Cellulose Benzoates. These derivatives, of which the mono-benzoate only may be said to be well characterized, result from the action of benzoyl chloride upon cellulose which has been previously modified, mercerized cotton and the cellulose regenerated from viscose being especially suitable. Cross,

cial value. At present these esters are but chemical curiosities.

1. Cross, Bevan and Briggs, Ber. 1905, **38**, 3531; abst. J.S.C.I. 1905, **24**, 1251; Zts. ang. Chem. 1906, **19**, 1267; Chem. Centr. 1905, **76**, 1625; Bull. Soc. Chim. 1906, (3), **36**, 639; Jahr. Chem. 1905-08, II, 986.

2. J.S.C.I. 1905, **24**, 374; abst. Zts. ang. Chem. 1905, **18**, 1988; Jahr. Chem. 1905-08, 975; Chem. Centr. 1905, **76**, 1702; J.C.S. 1905, **88**, 512.

3. D.R.P. 200334, 1907; abst. J.S.C.I. 1908, **27**, 1130; C.A. 1908, **2**, 2456; Mon. Sci. 1911, (5), **74**, 63; Chem. Zts. 1908, **7**, 909; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, 655; Jahr. Chem. 1905-08, 987; J.C.S. 1908, **94**, i, 955; Chem. Ind. 1908, **31**, 499; Wagn. Jahr. 1908, II, 363. For the formation of cellulose solutions by the action of concentrated cooled sulfuric acid upon cellulose, see E. Berl, F.P. 454753, 1913. D.R.P. 259248, 1912; abst. J.S.C.I. 1913, **32**, 653, 865. Belg. P. 253945, 1913; abst. Kunst. 1913, **3**, 355; C.A. 1913, **7**, 3026.

4. Example: 10 parts of ordinary bleached cotton is transformed into alkali-cellulose by means of zinc chloride and hydrochloric acid, is dissolved in 10% sodium hydroxide solution, so that a 5% solution by weight is formed. This solution is treated with 25 parts of *p*-toluol-sulfochloride. After about 20 hours the toluene-sulfonic ester of cellulose (toluolsulfocellulose) separates out as a white, amorphous powder, insoluble in acid zinc chloride solution or in cuproammonia, but dissolving in hot glacial acetic acid, epichlorhydrin, chloroform or ethyl acetate, the solution upon evaporation leaving a transparent pellicle.

Bevan and Beadle,[1] and Baumann,[2] have shown that the benzoates may be readily prepared by the above method, but it is difficult to obtain products of uniform composition. Benzoates from hydrocellulose[3] and from "soluble starch",[4] as well as the gelatinous hydrates precipitated from ammonio-cupric oxide-cellulose and from acid zinc chloride solutions,[5] give a higher benzoylation than does unmodified cellulose. Fibrous cellulose usually esterifies to a fibrous mono-benzoate. The systematic investigations of Skraup have shown[6] that when the reacting molecular proportions are $1OH:7NaOH:5C_6H_5COCl$, a complete or maximum esterification is insured.

More recently[7] O. Hauser and H. Muschner in investigating the conditions of the formation of cellulose benzoates by the action of benzoyl chloride upon cellulose and sodium hydroxide, were unable to obtain the fibrous cellulose monobenzoate insoluble in organic solvents and the soluble structureless dibenzoate as described by Cross and Bevan.[8] Briggs, however,[9] attributes their failure to the fact that the cellulose was first steeped in the benzoyl chloride and the mixture then shaken with caustic hydroxide, whereas the action of reagents upon the cellulose is to be reversed.[10]

1. Cross and Bevan, J.C.S. 1893, **26**, 837; Chem. News, 1890, **61**, 87. Cross, Bevan and Jenks, Ber. 1901, **34**, 2496.

2. Baumann, Ber. 1886, **19**, 3218.

3. Compt. rend. 1875, **81**, 1105; abst. Chem. Centr. 1876, 83; Jahr. Chem. 1875, 786; Bull. Soc. Chim. 1876, **26**, 190; J.C.S. 1876, **30**, 696.

4. J.C.S. 1899, **55**, 449; abst. Jahr. Chem. 1889, 2063; Mon. Sci. (4), **3**, 1284; Chem. Centr. 1889, 124; Bull. Soc. Chim. 1889, **2**, 682.

5. Chem. News, 1891, **63**, 66; abst. J.C.S. 1891, **60**, 690; Chem. Centr. 1891, **62**, 620; Jahr. Chem. 1891, 2181.

6. Monatsh. **10**, 389.

7. O. Hauser and H. Muschner, Zts. ang. Chem. 1913, **26**, 137; J.S.C.I. 1913, **32**, 357; Chem. Zentr. 1913, **84**, 1412; Jour. Dyers and Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C.A. 1913, **7**, 2854; J.C.S. 1913, **104**, i, 363.

8. Cross and Bevan, Ber. 1901, **34**, 1514; J.C.S. 1901, **80**, i, 452; Chem. Centr. 1901, **72**, II, 94; Jahr. Chem. 1901, 891.

9. J. Briggs, Zts. ang. Chem. 1913, **26**, 255; Chem. Zentr. 1913, **84**, 2110; Jour. Dyers Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C.A. 1913, **7**, 2855; J.S.C.I. 1913, **32**, 595; J.C.S. 1913, **104**, 594.

10. In order to control the velocity of the reaction and avoid wastage of the benzoyl chloride, it is advisable to introduce the moist alkali cellulose into a dilute solution of benzoyl chloride in an indifferent solvent, such as benzene. To obtain the fibrous diben-

H. Ost and F. Klein,[1] employing finely chopped cotton in their investigations upon the benzoylation of cotton by the Schotten-Baumann reaction, obtained a maximum yield of 218% of product when sodium hydroxide of 22.4% concentration is used in the moleular proportion of 30 of NaOH to 1 of cellulose, 22 molecules of benzoyl chloride being taken.[2]

In the A. Wohl process of manufacture[3] cellulose, as

zoate as the main product, cotton is steeped in 20% caustic soda lye, squeezed out and transferred to a 5% solution of benzoyl chloride in benzene. To obtain a maximum formation of the soluble tetrabenzoate, it is preferable to employ gelatinous hydrated cellulose, precipitated from viscose; this is brought into a state of semi-solution in caustic soda lye and the pasty mass is shaken with a 10% solution of benzoyl chloride. In any case, the analysis of the products without previous separation of the constituents is useless. The crude product is boiled with chloroform or acetic acid to extract the tetrabenzoate; the residue is exhausted repeatedly with strong cuprammonium reagent until all the unchanged cellulose is removed and the final residue is the fibrous dibenzoate. Either of these esters or the crude product itself may be further converted into mixed nitro-benzoic or aceto-benzoic esters soluble in organic media.

1. H. Ost and F. Klein, Zts. ang. Chem. 1913, **26**, 437; J.S.C.I. 1913, **32**, 823; Kunst. 1913, **3**, 331; C.A. 1913, **7**, 3661; J.C.S. 1913, **104**, i, 1043; Chem. Zentr. 1913, **85**, II, 1293.

2. With potassium hydroxide, a maximum yield of 211% of product was obtained with a lye of 31.4% concentration, the molecular proportions being the same as above. Up to the alkali concentrations mentioned, the yields of product regularly increased, without any sudden rise such as Vieweg has observed (J.S.C.I. 1907, **26**, 1157), and with higher concentrations the yields gradually decreased. By a second treatment similar to the first the yield of product may be increased, for instance a yield of 210% was increased to 224% after a second benzoylation. Fractional separation of the constituents of the products by solvents showed them to be highly complex mixtures. A mixture of aniline and phenol dissolves the esters containing 59% and over of combined benzoic acid; aniline alone dissolves those containing 61-65%, whilst chloroform dissolves only the higher esters containing 68-70% of benzoic acid. The highest benzoic ester obtained by the Schotten-Baumann method with repeated benzoylation contained 72.6% of benzoic acid, corresponding to a pentabenzoate on the C_{12} cellulose molecule. Esters containing up to 77% of benzoic acid, corresponding to a tribenzoate on the C_6 basis, were obtained by the Wohl method, by heating cellulose and pyridine with benzoyl chloride. The highest esters were obtained by working with a slight excess of the benzoyl chloride, e. g., in the molecular proportions $C_6H_{10}O_5+8C_5H_5N+4.8C_6H_5COCl$, whereby the mixture became slightly acid. The materials were heated for 3 hours at 120-130°. Such esters, however, gave brittle films, indicating incipient hydrolysis of the cellulose molecule.

3. D.R.P. 139669; abst. Jahr. Chem. 1903, 1014; Chem. Ind. 1903, **26**, 167; Wagn. Jahr. 1903, **49**, II, 418; Zts. ang. Chem. 1903, **16**, 285; Chem. Centr. 1903, I, 744. See also D.R.P. 243581, 1908;

tissue paper, is heated to 150° with benzoyl chloride in the presence of pyridine and a solvent as nitrobenzol. After esterification, the reaction mixture is poured into cold water, and the precipitated benzoic ester washed until neutral and dried at a moderate heat. It is stated by the patentess that upon evaporation of a chloroformic solution, a glossy and transparent film of di- and tri-benzoate remains which is insoluble in alcohol.

Cellulose monobenzoate (C_6 molecule) is highly resistant to solvents of cellulose and of the cellulose esters, and therefore may be freed from cellulose by treatment with the former, and from the higher benzoates by treatment with the latter. Pyridine, quinoline, phenol and nitrobenzene cause considerable swelling of fibrous monobenzoate, but without actual solution. Cellulose dibenzoate, even when prepared from fibrous cellulose, is devoid of structure, and its presence, therefore, in admixture with the fibrous monobenzoate is at once recognizable. It is insoluble in water, ethyl alcohol and ether, but is partially soluble in chloroform, tetrachlorethane, acetone, glacial acetic acid, nitrobenzene, pyridine, quinoline and phenol. Hot aniline, toluidine and xylidine have also a dissolving effect. Cellulose mono-*p*-chlorobenzoate,[1] prepared from hydrocellulose and *p*-chlorobenzoyl chloride is an amorphous, non-fusible, non-hygroscopic white powder, insoluble in all solvents. Nitration of the cellulose benzoates leads to the formation of cellulose dinitrate-dinitrobenzoate and cellulose trinitrate-dinitrobenzoate, which, as yet possess only a theoretical interest.

abst. J.S.C.I. 1912, **31**, 381; C.A. 1912, **6**, 2316; Chem. Tech. Rep. 1912, **36**, 196; Wagn. Jahr. 1912, II, 17; Zts. ang. Chem. 1912, **25**, 654; Chem. Ind. 1912, **35**, 190; Chem. Zentr. 1912, **83**, 695. E.P. 2527, 1912. A Nastjukoff (Jour. Russ. Phys. Chem. Soc. 1902, **34**, 231, 505; abst. Chem. Centr. 1902, I, 1277; II, 576; Jahr. Chem. 1902, 1054, 1142; J.C.S. 1902, **82**, i, 362, 747; Bull. Soc. Chim. 1902, (3), **28**, 130, 481), has described a tetraphenyl cellulose, prepared by allowing benzol to act upon a solution of cellulose in concentrated sulfuric acid. By addition of ice a sulfurated tetraphenyl derivative is precipitated, insoluble in all solvents, but which, like cellulose, gives nitro products.

1. O. Hauser and H. Muschner, Zts. ang. Chem. 1913, **26**, 137; abst. Chem. Zentr. 1913, **84**, I, 1412; J.C.S. 1913, **104**, i, 363; C.A. 1913, **7**, 2854.

A. Luck [1] has patented an explosive, in which the brisant effect of the cellulose nitrate is modified by the presence of other cellulose esters, as the benzoate. The trade name of "benzoale" has been given to the article.

The Akt-Ges. fur Anilin-Fabrikation [2] prepare cellulose benzoate by combining 2.4 parts benzoic anhydride, 6 parts glacial acetic acid, 0.2 parts bromine with ½ parts hydrocellulose, the temperature being around 50°. The benzoic esters have been proposed for the insulation of wire and the protection of metal surface [3 4] as plastic bodies in conjunction with chloral and amyl lactate.[5]

1. E.P. 24662, 1898; abst. J.S.C.I. 1900, **19**, 375.
2. E.P. 22237, 1911; abst. J.S.C.I. 1912, **31**, 279. F.P. 435507, 1911; abst. J.S.C.I. 1912, **31**, 329. Belg. P. 239564, 1911.
3. F.P. 375092, 1907; abst. J.S.C.I. 1907, **26**, 877.
4. U.S.P. 695127, 1902; Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303.
5. U.S.P. 999490, 1911; abst. J.S.C.I. 1911, **30**, 1051.

CHAPTER III.

CELLULOSE ACETATE SOLVENTS.

In the decade following the discovery of the cellulose nitrates by Schoenbein in 1846, over six hundred original contributions were published on the subject, whereas in the period of twice that time after Schuetzenberger announced in 1869 his preliminary experiments on the acetation of cotton, less than one-fourth that number of papers have appeared relating to the corresponding acetic esters. This significant comparison is mainly attributable to the fact that the cellulose nitrates in their dry form have many commercial uses, both in war and in the peaceful arts, while at the present time, as in the past, there have been no industrial uses in which dry or undissolved cellulose acetate may be employed with profit. It follows, therefore, that the question of solvents is comparatively of much greater and far-reaching importance in the expansion of the cellulose acetate art, than in the older, better known, and more highly developed nitrocellulose industry.

The early endeavors to utilize nitrocellulose in solution were disappointing, mainly on account of too few and too hygroscopic solvents. Commencing with the early endeavors of A. Parkes in 1855,—when methyl alcohol and ether were the best known of the light boiling liquids, and nitrobenzene the only satisfactory fluid of high boiling point,—a careful analysis of pyroxylin development from that time to the present, will impress upon one the fact that industrial expansion occurred only at those periods when someone discovered valuable solvents, or devised improved ways of combining them. And it appears clear that the present most fruitful field for the technical extension of the non-explosive and relatively non-inflammable esters of cellulose, is in the discovery, extension and utilization of the number of simple

and compound direct and indirect solvents, and bodies inducing thermoplasticity.

Solubility determinations of the acetic esters of cellulose are much more confusing than with the corresponding nitrates, for the partial hydration of the acetates, which gives rise to a great number of products with distinct variations in solubility, finds no corresponding analogue with the nitrocelluloses. For this reason solubility determinations of various investigators have shown a marked discrepancy and lack of uniformity, and attempts to classify and correlate into a comprehensive and logical system, the scattered results of the solubility of the various cellulose acetates in different media, is exceedingly difficult at the present time, if not substantially impossible.

As A. Eichengruen has pointed out, undoubtedly a whole series of esters analytically indistinguishable from the normal triacetate exists, and the preponderance of one or more of these esters in a mixture may exert an influence entirely out of proportion to the amount present. Investigators have long since shown the fallacy of attempting to judge of the ether-alcohol solubility of a cellulose nitrate from the nitrogen content alone, for endeca-nitrocelluloses have been described which were entirely insoluble and which dissolved without difficulty in ether-alcohol. It is quite probable that similar difficultly explainable phenomena are incorporated in the recorded soubility determinations of the acetic esters, which makes generalizations difficult if not impossible. The subject is also greatly complicated by the phenomena of partial hydration after acetation, where a whole range of undoubtedly distinct chemical individuals is comprehended within the range of those esters in which solubility in chloroform gradually decreases until a point of solubility represented by incipient plasticity in cold or warm chloroform results, while at the same time the corresponding solubility in absolute acetone gradually increases, until an ester plastic in cold chloroform will be found to entirely dissolve in absolute acetone. Hydration continued beyond this point results in

products of decreased commercial value soluble in acetone containing larger amounts of water, until substances soluble in benzene, the petroleum benzines and finally pure water result, the latter being commercially worthless. Coincident with hydration is loss of acetic acid, but the stages are indistinguishable, and the solubility results are not always dependent upon the acetic acid content. Hydrolysis of the cellulose aggregate in the ester appears to take place coincident with elimination of acetic acid, so that two variables are simultaneously introduced.

The majority of the solubility determinations found in the literature are practically worthless for systematic generalizations, because the nature of the normal or hydrated acetylcellulose operated upon is not stated, or the conditions under which the determinations were made not recorded.

It is difficult to rationally group the known cellulose acetate solvents according to their chemical classification. For instance, aniline is an excellent solvent of the partially hydrated cellulose acetate which dissolves in acetone, whereas monomethylaniline, monoethylaniline or dimethylaniline under the same conditions are practically devoid of dissolving power. The excellent solvent power of tetrachlorethane is not shown by pentachlorethane or trichlorethane, and in a much reduced degree by acetylidene tetrachloride, the isomer of tetrachlorethane (acetylene tetrachloride). The solubility of cellulose triacetate in chloroform and its insolubility in carbon tetrachoride is another familiar example. Generalizations from chemical composition or constitution alone are therefore apt to be misleading.

It is noticeable, however, that the acetic esters of various alcohols are active solvents or plastic or softening agents of the cellulose acetates, especially those partially hydrated modifications soluble in absolute actone. For instance, of the monohydric, aliphatic alcohols combined with acetic acid, methyl and ethyl acetate are excellent solvents, while the corresponding carbocyclic monohydric alcoholic acetic esters, benzyl acetate and phenyl acetate, have likewise distinct

dissolving power. Of the dihydric alcohols, glycol diacetate of the aliphatic series, and resorcinol diacetate of the aromatic, are both heavy oils and dissolve cellulose acetate readily. The trihydric aliphatic alcoholic ester, glyceryl triacetate, and pyrogallol triacetate, the corresponding aromatic ester, dissolve cellulose acetate with avidity, the latter in the presence of acetone. Of the tetrahyroxyl alcohols, erythrol forms a tetracetate which melts at 85°, while hexaoxybenzene forms a hexacetyl derivative, both being plastic-inducing bodies in conjunction with direct solvents. The observation that the acetic esters of monohydric and polyhydric alcohols are solvents of acetated cellulose, is similar to the generalization of the solubility of the corresponding nitric esters for nitrated cellulose. For example, nitrated glycerol dissolves nitrocellulose, and acetated glycerol is a solvent for acetated cellulose. Ethylene glycol nitrate dissolves nitrocellulose, and ethylene glycol acetate that of acetylcellulose.

Conversely, classification by groups is of advantage as suggesting other members of homologous or isologous series, isomers, polymers or related bodies, which may impart the physical or solvent properties desired. This is especially noticeable in plastic-inducing solids, where one member of a series may impart greatly differing properties from that induced to a compound of the same series. For this reason, therefore, those dissolving bodies which have been proposed from time to time as especially applicable to the cellulose acetates, will, as far as practicable, be recorded herewith according to their composition as falling into the general groups of alcohols, ethers, ketones, aldehydes, acids and esters, the simple solvents and plastic-inducing bodies being described together.

Alcohols. Ethyl alcohol is a non-solvent of not hydrated triacetylcellulose, but as hydration proceeds beyond the point of solubility in absolute acetone, solubility in absolute ethyl alcohol commences, and as hydration proceeds, acetic acid is split off and esters formed which become soluble in ethyl alcohol containing increasing amounts of water. Ethyl

alcohol has frequently been described as a cellulose acetate precipitating agent,[1] and processes for the preparation of alcohol-soluble cellulose acetates are many,[2] either absolute or as low in alcohol as 70% [3] or 75% [4] being employed. Esters

1. D.R.P. 222450, 1908; abst. J.S.C.I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Chem. Zentr. 1910, **81**, 48; Wagn. Jahr. 1910, **56**, II, 434; Chem. Zts. 1910, **9**, 1902; C.A. 1910, **4**, 2875. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, **60** [(4), **17**], 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. **60**, [(4), **17**], 54. Aust. P. 31391. It. P. 62042, 1901. E.P. 7341, 1903; abst. J.S.C.I. 1904, **23**, 501. F.P. 330714, 1903; abst. J.S.C.I. 1903, **22**, 1100; Mon. Sci. 1904, (4), **60**, 66. U.S.P. 627031, 1899. E.P. 18283, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 62188, 1899. F.P. 282320, 1899. Russ. P. 3378, 1900. Dan. P. 2636, 1899. Luxem. P. 3302, 3361, 7610, 1899. Port. P. 2899, 1899. Belg. P. 138462, 1898. Add. to Belg. P. 137577. Hung. P. dated Aug. 31 and Nov. 8, 1898. Norw. P. 7610, 1898.

2. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, **60**, [(4), **17**], 173. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, **60**, [(4). **17**], 54. Aust. P. 31391. It. P. 62042, 1901. D.R.P. 222450, 1908; abst. J.S.C.I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Wagn. Jahr. 1910, **56**, II, 434; Chem. Zentr. 1910, **81**, 48; Chem. Zts. 1910, **9**, 1902. C.A. 1910, **4**, 2875. E.P. 19735, 1908; abst. J.S.C.I. 1910, **29**, 18. F.P. 393963, 1908; abst. J.S.C.I. 1909, **23**, 257. D.R.P. 223793, 1907; being Add. to D.R.P. 210519. Aust. P. 51094, 1908. D.R.P. 237151, 1908; abst. J.S.C.I. 1911, **30**, 1232; Zts. ang. Chem. 1911, **24**, 1838; Chem. Zentr. 1911, **82**, 500. The Internationale Celluloseester Ges. (D.R.P. 242289, 1910; abst. Zts. ang. Chem. 1912, **25**, 286; Chem. Zentr. 1912, I, 298; Chem. Tech. Rep. 1912, **36**, 47; Wagn. Jahr. 1912, II. 17; Chem. Zts. 1912, **11**, No. 2798; C.A. 1912, **6**, 2170), separate cellulose esters from solutions, especially from crude esterifying mixtures, by means of ethyl alcohol as a precipitant. See also D. R. Anm. I.-14379 of 1912, and the Internationale Celluloseester Ges. and E. Bronnert, D. R. Anm. B.-71109, 1913; abst. Kunst. 1913, **3**, 400.

3. U.S.P. 809935, 1906; abst. J.S.C.I. 1906, **25**, 195; Mon. Sci. 1906, (4), **64**, 120. D.R.P. 185837, 1902; Add. to D.R.P. 159524; abst. Chem. Ind. 1907, **30**, 313; Chem. Tech. Rep. 1907, **31**, 302; Zts. ang. Chem. 1908, **21**, 269; Chem. Zentr. 1907, **78**, 654; Jahr. Chem. 1905-08, 984. First Add. 1425 dated Jan. 30, 1903, to F.P.

soluble in 70% alcohol, however, have but little strength for film formation or filament manufacture. M. Althausse[1] has described the manufacture of hydrocellulose acetates which dissolve in alcohol. For toughening incandescent mantles, a mixture of cellulose acetate, camphor and castor oil dissolved in alcohol have been patented.[2] Toluene and alcohol,[3] dichlorethylene and alcohol,[4] and pentachlorethane and alcohol,[5] are examples of combinations of two non-solvents inducing solution or gelatinization. Monoacetylethylaniline and alcohol[6] forms a thermoplastic compound with acetone-soluble cellulose acetate, which is moldable at the temperature of boiling water.

317007; abst. J.S.C.I. 1903, **22**, 1015. E.P. 7346, 1903; abst. J.S.C.I. 1904, **23**, 337. Aust. P. 32637.

4. F.P. 432046, 1911; abst. J.S.C.I. 1912, **31**, 24. E.P. 20978, 1911; 20852, 21376, 1912; abst. J.S.C.I. 1913, **32**, 133. Belg. P. 241250, 246250, 246251, 1912. Aust P. 12o, Mar. 16, 1910; Mar. 9, 1911.

1. U.S.P. 679204, 1901; abst. Mon. Sci. 1901, (4), **57**, 284. F.P. 304723, 1900; abst. J.S.C.I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1900, (4), **59**, 20. D.R.P. 123121, 1900; abst. J.S.C.I. 1901, **20**, 1133; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, II, 567; Mon. Sci. 1900, (4), **59**, 9; Jahr. Chem. 1901, 892. E.P. 19039, 1900; abst. J.S.C.I. 1901, **20**, 926. U.S.P. 692497, 1902; abst. J.S.C.I. 1902, **21**, 362; Mon. Sci. 1902, (4), **58**, 161. F.P. 308506, 1901; abst. J.S.C.I. 1902, **21**, 64; Mon. Sci. 1902, (4), **58**, 159.

2. F.P. 324718, 1903; abst. J.S.C.I. 1903, **22**, 620.

3. U.S.P. 1015155, 1912; abst. C.A. 1912, **6**, 684; Mon. Sci. 1912, **77**, 163. Swiss. P. 52437; abst. Kunst. 1912, **2**, 135. It. P. 47889.

4. U.S.P. 1015156, 1912; abst. Mon. Sci. 1912, **77**, 173. E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1005; Chem. Tech. Rep. 1911, **35**, 340. E.P. 18076, 1910, being First Add. to E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1199. F.P. 412797, 1910; abst. Rev. Chim. Ind. 1910, **21**, 257; J.S.C.I. 1910, **29**, 1199. First Add. 12388, Mar. 19, 1910, to F.P. 412797; abst. J.S.C.I. 1910, **29**, 1199. D.R.P. 238348, 1909; abst. C.A. 1912. **6**, 1672; Chem. Zentr. 1911, **82**, 1085; Chem. Ind. 1911, **34**, 637; Chem. Tech. Rep. 1911, **35**, 520. Aust. P. 47899; Swiss. P. 52115; abst. Kunst. 1912, **2**, 99. Can. P. 129265, 1910. U.S.P. 988965, 1911; abst. J.S.C.I. 1911, **30**, 616; C.A. 1911, **5**, 2176; Mon. Sci. 1912, **77**, 30. E.P. 16932, 1910; abst. J.S.C.I. 1910, **29**, 1299; Chem. Tech. Rep. 1911, **35**, 35. F.P. 418309, 1910; abst. J.S.C.I. 1911, **30**, 80. Aust. P. 5592, July 11, 1910.

5. E.P. 14364, 1910; abst. J.S.C.I. 1910, **29**, 1152. D.R.P. Anm. F. 28111, of Aug. 25, 1909; refused Feb. 20, 1911. Aust. P. 46991, 1910. Swiss. P. 52438; abst. Kunst. 1912, **2**, 135. F.P. 417250, 1910; abst. J.S.C.I. 1911, **30**, 19.

6. F.P. 427804, 1910; abst. J.S.C.I. 1911, **30**, 1051; C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 111.

F. Bayer & Co.[1] have described the preparation of alocholic solutions of acetylcellulose in which the latter are dissolved in alcohol in the presence of zinc chloride or potassium or ammonium sulfocyanide. Such solutions remain liquid at the room temperature, may be spread with a brush as ordinary varnish, and on account of the relatively low volatility of the solvents there is comparatively no odor from the coating. The thiocyanates and zinc chloride, which have a hygroscopic action on the coating, may be washed out readily with water. These solutions are said to be especially useful for spinning, water forming the precipitant from which the alcohol and salts may be readily recovered. Camphor substitutes, dyes or pigments may be added to the solutions without detrimental effect. In a later patent[2] stannic chloride or antimony trichloride are specified. Ten parts of acetylcellulose added to 40 parts of stannic chloride in 60 parts of alcohol results in the formation of a clear solution.

Methyl alcohol is a solvent of some modifications of acetylcellulose,[3] and in conjunction with tetrachlorethane[4] forms a widely used solvent combination, which in film formation exerts a temporary suppleness and plasticity. Amyl alcohol has been proposed as a diluent,[5] but it has no dissolving effect. Amyl alcohol mixed with 60% amyl acetate forms an excellent gelatinizing medium for chloroform-soluble and not-hydrated cellulose esters. Benzyl alcohol, chloro-

1. D.R.P. 256922, 1911; abst. C.A. 1913, **7**, 2116; Kunst. 1914, **4**, 35; Zts. ang. Chem. 1913, **26**, 290; Chem. Zentr. 1913, I, 1156.

2. D.R.P. 268627, 1911, being Add. to D.R.P. 256922; abst. C.A. 1914, **8**, 2060; Kunst. 1914, **4**, 20. See also A. Eichengruen, D.R.P. 254385, 1909; abst. C.A. 1913, **7**, 1288; Zts. ang. Chem. 1913, **26**, 32; Chem. Zentr. 1913, I, 361.

3. F.P. 354942, 1905; abst. J.S.C.I. 1905, **24**, 1169. Add. dated June 8, 1905, to F.P. 354942; abst. J.S.C.I. 1905, **24**, 1226. E.P. 12277, 12278, 1905; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185240, 1906; abst. Zts. ang. Chem. 1907, **20**, 2177; Chem. Zentr. 1907, II, 1037. D.R.P. 185241, 1906, Add. to D.R.P. 185240; abst. Chem. Zentr. 1907, II, 1819.

4. U.S.P. 1009116, 1911; abst. J.S.C.I. 1911, **30**, 1447; Mon. Sci. 1912, **77**, 163. F.P. 417319, 1910; abst. J.S.C.I. 1911, **30**, 19; Mon. Sci. 1913, **78**. 30.

5. E.P. 14293, 1910; abst. J.S.C.I. 1911, **30**, 1171.

benzyl alcohol,[1] pyrocatechin, its isomer resorcin,[2] its monomethyl ether, guaiacol, and dimethyl ether, veratrol, have been described by H. Danzer as plastic-inducing bodies, with or without the addition of small amounts of alcohol and camphor. This inventor has also patented the use of *a*-naphthol, *b*-naphthol, ethyl-*b*-naphthol, methyl-*a*-naphthol, tri-chlorphenol, the trihydric alcohol pyrogallol, and the diolefine phenols, safrol and *iso*-safrol. Safrol, a pleasant smelling liquid boiling at 232°, and *iso*eugenol boiling at 260°, have been used as nitrocellulose solvents.[3] Anethol, eugenol and apiol are olefine phenols of considerable dissolving power, but at present too costly for commercial work. Of the dihydric aliphatic alcohols the glycols are too expensive, are partially soluble in water and hygroscopic; the trihydric alcohols being readily miscible with water in any proportion and also highly hygroscopic.[4] Glycerol-soluble cellulose acetates have been described by C. Claessen,[5] but a cellulose acetate which has been hydrated so far as to dissolve in glycerol is worthless for film manufacture. As a plastic-inducing body[6] or cellulose ester diluent,[7] glycerol is much inferior to its acetic esters, especially glyceryl triacetate (acetin). A textile

1. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 433264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

2. U.S.P. 1005454, 1911; abst. J.S.C.I. 1911, **30**, 1249. E.P. 476, 1910; abst. J.S.C.I. 1910, **29**, 1082. F.P. 411298, 1910; abst. J.S.C.I. 1910, **29**, 978; Phot. Ind. 1910, 1221; Eders Jahr. 1911, 526. Aust. P. 50656, 1910; abst. Kunst. 1912, **2**, 77. Phot. Ind. 1911, **28**; Eders Jahr. 1911, 526. Belg. P. 222106, 1910. Hung. Anm. M. 3691, Dec. 30, 1909. Swiss. P. 51839, 1910; abst. Kunst, 1912, **2**, 77.

3. U.S.P. 503402, 1893.

4. For method of producing butylene glycol, see U.S.P. 1008333, 1911; E.P. 4099, 17259, 1911; abst. J.S.C.I. 1911, **30**, 1470; 1912, **31**, 257.

5. D.R.P. 222450, 1908; abst. J.S.C.I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Wagn. Jahr. 1910, **56**, II, 434; Chem. Zentr. 1910, **81**, 48; Chem. Zts. 1910, **9**, 1902; C.A. 1910, **4**, 2875.

6. F.P. 354942, 1905; abst. J.S.C.I. 1905, **24**, 169. Add. dated June 8, 1905, to F.P. 354942; abst. J.S.C.I. 1905, **24**, 1226. E.P. 12277, 12278, 1905; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185240, 1906; abst. Zts. ang. Chem. 1907, **20**, 2177; Chem. Zentr. 1907, **78**, 1037. D.R.P. 185241, 1906. Add. to D.R.P. 185240; abst. Chem. Zentr. 1907, **78**, 1819.

7. E.P. 26657, 1909; abst. J.S.C.I. 1910, **29**, 1152. F.P. 421010, 1910; abst. J.S.C.I. 1911, **30**, 416.

printing composition has been placed on the market by F. Bayer & Co. for use with cellulose acetate which has been hydrated to the point represented by solubility in 40% aqueous acetic acid.[1] In acetic photographic emulsions, the addition of small amounts of glycerol induces suppleness and a decreased tendency of the solidified emulsion to peal.[2] Chloral alcoholate[3] melting at 65° and boiling at 114-115°, has the disadvantage of gradually reverting to chloral hydrate when brought in contact with water.

Of the carbocyclic alcohols, phenol (carbolic acid) was early used, both as a solvent with sufficient water to liquify it,[4] and as a plastic when melted in the crystalline form with cellulose acetate. Not-hydrated esters will dissolve in phenol by aid of a gentle heat,[5] to produce moldable bodies. In the process of Koller,[6] 2 parts of phenol is mixed with 20 parts of tri- or per-chlorethylene and 1 part of cellulose acetate added. After the mass has become homogeneous and the ester passed entirely into solution, perchlorethylene is evaporated until the plastic has acquired the desired consistency. L. Lederer prepares artificial filaments[7] by discharging an acetic or phenol solution of acetylcellulose into benzine or ligroin as the precipitant. Plastics of cellulose acetate, phenol and casein,[8] or albumen,[9] or formalin have been described,

1. F.P. 341007, 1904; abst. J.S.C.I. 1904, **23**, 864.

2. E.P. 26503, 1906; abst. J.S.C.I. 1907, **26**, 1295. F.P. 371358, 1906; abst. J.S.C.I. 1907, **26**, 344; Mon. Sci. 1908, **69**, 50. D.R.P. 191326, 1906. Belg. P. 195837, 1906.

3. E.P. 26657, 1909; abst. J.S.C.I. 1910, **29**, 1152. F.P. 421010, 1910; abst. J.S.C.I. 1911, **30**, 416.

4. E.P. 10243, 1903; abst. J.S.C.I. 1904, **23**, 557 F.P. 385 179, 1907; abst. J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 105; Bull. Soc. Chim. 1909, (4), **6**, 557. F.P. 385180, 1907; abst. J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 106; Bull. Soc. Chim. 1909, (4), **6**, 557.

5. U.S.P. 774713, 1904; abst. J.S.C.I. 1904, **23**, 1159; Mon. Sci. 1905, (4), **62**, 50. U.S.P. 774714, 1904; abst. J.S.C.I. 1904, **23**, 1159.

6. E.P. 4744, 1911; abst. J.S.C.I. 1912, **31**, 328; C.A. 1912, **6**, 2315; F.P. 440133, 1912; abst. J.S.C.I. 1912, **31**, 680; Kunst. 1912, **2**, 355, 439. U.S.P. 1079773, 1913; abst. J.S.C.I. 1913, **32**, 1153.

7. E.P. 7341, 1903; abst. J.S.C.I. 1904, **23**, 501. F.P. 330714, 1903; abst. J.S.C.I. 1903, **22**, 1100; Mon. Sci. 1904, (4), **60**, 66.

8. F.P. 441146, 1911; abst. J.S.C.I. 1912, **31**, 845; Kunst. 1912, **2**, 355. F.P. 354942. 1905; abst. J.S.C.I. 1905, **24**, 1169. Add. dated June 8, 1905, to F.P. 354942; abst. J.S.C.I. 1905, **24**, 1226.

but they appear, as yet, not to have entered into commerce. As a softening body to increase pliability and suppleness [1] phenol in combination is often useful.[2] Trichlorphenol, nitrophenol and tribromphenol give colored compounds, or plastics which become acid upon standing. The cresols [3] differ but little in their action on cellulose acetate from the phenols Amidophenol in combination and saligenin has been patented by L. Lederer for the manufacture of artificial horn.[4] Thymol (methylisopropyl phenol) and its isomer carvacrol, have been used in combination with cellulose acetate either as a softener,[4] or in conjunction with casein as a thermoplastic.[5] In

E.P. 12277, 12278, 1905; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185 240, 1906; abst. Chem. Tech. Rep. 1907, **31**, 361; Wagn. Jahr. 1907, II, 563; Zts. ang. Chem. 1907, **20**, 2177; Chem. Zentr. 1907, II, 1037. D.R.P. 185241, 1906. Add. to D.R.P. 185240; abst. Chem. Zentr. 1907, **78**, 1819; Chem. Tech. Rep. 1907, **31**, 396; Wagn. Jahr. 1907, II, 563.

9. U.S.P. 952724, 1910; abst. J.S.C.I. 1910, **29**, 503. E.P. 4145, 1909; abst. J.S.C.I. 1910, **29**, 100. F.P. 402028, 1909; abst. J.S.C.I. 1909, **28**, 1212. D.R.P. 242467, 1908; abst. Kunst. 1912, **2**, 59. C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 111.

1. U.S.P. 695127, 1902. Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303. U.S.P. 712200, 1902; Mon. Sci. 1903, (4), **60**, 165.

2. U.S.P. 774677, 1904; abst. J.S.C.I. 1904, **23**, 1159. E.P. 7088, 1902; abst. J.S.C.I. 1903, **22**, 563, F.P. 319724, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Add. 811 dated Mar. 18, 1902, to F.P. 319724; abst. J.S.C.I. 1903, **22**, 563. D.R.P. 145106, 1902; abst. Jahr. Chem. 1904, 1168; Mon. Sci. 1904, (4), **60**, 93; Zts. ang. Chem. 1903, **16**, 1090; Chem. Centr. 1903, II, 1155. D.R.P. 151918, 1902. Add. to D.R.P. 145106; abst. Chem. Centr. 1904, II, 1180; Jahr. Chem. 1904, 1168. D.R.P. 152111, 1902. E.P. 27258, 1910; abst. J.S.C.I. 1911, **30**, 1112; C.A. 1912, **6**, 1526. F.P. 419530, 1910; abst. J.S.C.I. 1911, **30**, 205. First Add. 13237, dated Sept. 29, 1911, to F.P. 419530; abst. J.S.C.I. 1911, **30**, 415. D.R.P. 145106. Can. P. 129983.

3. F.P. 432264. 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911. U.S.P. 774713, 1904; abst. J.S.C.I. 1904, **23**, 1159; Mon. Sci. 1905, (4), **62**, 50. U.S.P. 774714, 1904; abst. J.S.C.I. 1904, **23**, 1159.

4. U.S.P. 774677, 1904; abst. J.S.C.I. 1904, **23**, 1159. E.P. 7088, 1902; abst. J.S.C.I. 1903, **22**, 563. F.P. 319724, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Add. 811 dated Mar. 18, 1902, to F.P. 319724; abst. J.S.C.I. 1903, **22**, 563. D.R.P. 145106, 1902; abst. Jahr. Chem. 1904, 1168; Mon. Sci. 1904, (4), **60**, 93; Zts. ang. Chem. 1903, **16**, 1090; Chem. Centr. 1903, II, 1155; Wagn. Jahr. 1904, II, 512. D.R.P. 151918, 1902. Add. to D.R.P. 145106, 1902; abst. Chem. Centr. 1904, II, 1180; Jahr. Chem. 1904, 1168. D.R.P. 152111, 1902.

the nitrocellulose industry,[1] thymol has been used in plastics to lower the melting point of camphor.

Both *a*-naphthol and *b*-naphthol dissolve acetated cellulose in the presence of a small amount of ethyl alcohol either alone [2] or with varying amounts of casein.[3] The great drawback to the use of the naphthols is their distinctive and persistent odor, even when present in comparatively small amounts. Cyclopentanol,[4] and cyclohexanol [5] are useful solvents in conjunction with acetone and alcohol, both for the nitric and acetic esters of cellulose, benzhydrol,[6] diphenylcarbinol and saligenin [7] have been patented. Many of these alcohols upon esterification—especially acetation—yield esters which are powerful direct solvents for acetylcellulose, and

4. U.S.P. 712200, 1902; abst. Mon. Sci. 1903, (4), **60**, 165.

5. F.P. 354942, 1905; abst. J.S.C.I. 1905, **24**, 1169. Add. dated June 8, 1905, to F.P. 354942; abst. J.S.C.I. 1905, **24**, 1226. E.P. 12277, 12278, 1905; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185 240, 1906; abst. Zts. ang. Chem. 1907, **20**, 2177; Chem. Zentr. 1907, **78**, 1037. D.R.P. 185241, 1906. Add. to D.R.P. 185240; abst. Chem. Zentr. 1907, **78**, 1819.

1. U.S.P. 572134, 1896.

2. E.P. 27258, 1910; abst. J.S.C.I. 1911, **30**, 1112; C.A. 1912, **6**, 1526. F.P. 419530, 1910; abst. J.S.C.I. 1911, **30**, 205. First Add. 13237, dated Sept. 29, 1911, to F.P. 419530; abst. J.S.C.I. 1911, **30**, 415. D.R.P. 145106. Can. P. 129983.

3. F.P. 354942, 1905; abst. J.S.C.I. 1905, **24**, 1169. Add. dated June 8, 1905, to F.P. 354942; abst. J.S.C.I. 1905, **24**, 1226. E.P. 12277, 12278, 1906; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185240, 1906; abst. Zts. ang. Chem. 1907, **20**, 2177; Chem. Zentr. 1907, **78**, 1037. D.R.P. 185241, 1906. Add. to D.R.P. 185240; abst. Chem. Zentr. 1907, **78**, 1819.

4. F.P. 440733, 1912; abst. J.S.C.I. 1912, **31**, 828; Kunst. 1912, **2**, 414; 1913, **3**, 17. E.P. 3869, 7292, 1912; abst. J.S.C.I. 1912, **31**, 1176. D.R.P. 251351, 1911; abst. C.A. 1913, **7**, 351, 427, 1426; Chem. Tech. Rep. 1912, **36**, 584; Chem. Ind. 1912, **35**, 657; Zts. ang. Chem. 1912, **25**, 2508; Chem. Zentr. 1912, **83**, 1246; Farben Ztg. 1912, **17**, 2815; J.S.C.I. 1912, **31**, 1191. D.R.P. 255692, 1912; abst. C.A. 1913, **7**, 1815; Kunst. 1913, **3**, 20. U.S.P. 1045895, 1912; abst. J.S.C.I. 1913, **32**, 19.

5. F. Raschig, U.S.P. 900204, 1908. D.R.P. 174914, 1905; Chem. Centr. 1906, II, 1702; Jahr. Chem. 1905-08, II, 993; Zts. ang. Chem. 1907, **20**, 369; Chem. Zts. 1907, **6**, 9; Wagn. Jahr. 1906, 527.

6. F.P. 432264, 1911; abst. J.S.C.I. 1912. **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264, 1911; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

7. E.P. 27258, 1910; abst. J.S.C.I. 1911, **30**, 1112; C.A. 1912, **6**, 1526. F.P. 419530, 1910; abst. J.S.C.I. 1911, **30**, 205. First Add. 13237, dated Sept. 29, 1911, to F.P. 419530; abst. J.S.C.I. 1911, **30**, 415. D.R.P. 145106. Can. P. 129983.

many, being of a heavy viscous nature, of high boiling point and low volatility, produce excellent softening effects on acetate sheets, ribbons and films.

Ethers. Dimethyl, methyl-ethyl, and diethyl ethers are all non-solvents of normal and partially hydrated acetylcellulose. C. Claessen [1] has described cellulose acetates entirely insoluble in diethyl ether. It has been proposed as a diluent in the acetylating bath,[2] but the boiling point (35°) is lower than the normal maximum temperature of acetation, and hence is valueless in this connection. Diethyl ether may be prepared according to the process of G. Benjamin [3] by subjecting a mixture of ethyl hydrogen sulfate, ethylene, hydrogen and oxygen to the action of heat, and when thus prepared in the crude state, is said to dissolve some forms of the partially hydrated ester. Methylated ether is a non-solvent,[4]

1. D.R.P. 222450, 1908; abst. J.S.C.I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Wagn. Jahr. 1910, **56**, II, 434; Chem. Zentr. 1910, **81**, 48; Chem. Zts. 1910, **9**, 1902; C.A. 1910, **4**, 2875. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, **60**, [(4), **17**], 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870; F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, **60**, [(4), **17**], 54. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. Aust. P. 31391. It. P. 62042, 1901.

2. U.S.P. 812098, 1906; abst. J.S.C.I. 1906, **25**, 232; Mon. Sci. 1906, (4), **64**, 120. E.P. 24083, 1904; abst. J.S.C.I. 1905, **24**, 1081. F.P. 347906, 1904; abst. J.S.C.I. 1905, **24**, 454; Mon. Sci. 1906, (4), **64**, 15; Chem. Ztg. 1905, **29**, 493. D.R.P. 184145, 1904; abst. Chem. Zentr. 1907, **78**, 365; Mon. Sci. 1909, (4), **70**, 77; Jahr. Chem. 1905-08, 983; Zts. ang. Chem. 1908, **21**, 268; Chem. Ind. 1907, **30**, 238. D.R.P. 184201, 1904; abst. Zts. ang. Chem. 1908, **21**, 268; Chem. Zentr. 1907, **78**, 365; Mon. Sci. 1909, (4), **70**, 77; Jahr. Chem. 1905-08, 984; Zts. ang. Chem. 1908, **21**, 268; Chem. Ind. 1907, **30**, 238. 216, 1905. Swed. P. 20249, 1905. Russ. P. 11492, 1907. D.R.P. 237151, 1908; abst. J.S.C.I. 1911, **30**, 1232; Zts. ang. Chem. 1911, **24**, 1838; Chem. Zentr. 1911, **82**, 500. D.R.P. 242289, 1910; abst. C.A. 1912, **6**, 2170; Kunst. 1913, **3**, 35; Chem. Zts. 1912, **11**, 2798; Chem. Tech. Rep. 1912, **36**, 47; Zts. ang. Chem. 1912, **25**, 286; Chem. Ind. 1912, **35**, 87; Chem. Zentr. 1912, **83**, 298.

3. E.P. 14233, 1899; abst. J.S.C.I. 1902, **21**, 364. Methylene dimethyl ether (methylal), and pyrocatechin monoethyl ether (guaethol, thanatol, ajacol) with ethyl alcohol are permanent solvents of acetone-soluble acetylcellulose.

4. E.P. 14293, 1910; abst. J.S.C.I. 1911, **30**, 1171.

monochlor- and dichlor-ether, boiling at 98° and 145° respectively, have a slight solvent effect on alcohol-soluble esters. Mesityl oxide is an excellent nitrocellulose solvent, and a gelatinizing agent for acetylcellulose, especially in conjunction with other liquids. It is ethereal smelling, insoluble in water, miscible with alcohol, ether, chloroform, acetylene tetrachloride and amyl acetate, boils at about 129°, and may be distilled without change.

Of the carbocyclic ethers, methyl-phenyl ether (anisol), ether-phenyl ether (phenetol), diphenyl ether, chlor and dichlor-phenetol, nitroanisol, and chlornitroanisol have been patented by H. Dreyfus [1] as acetate solvents and plastic-inducing bodies. Alone they are weak solvents, their dissolving power being materially increased by the addition of ethyl alcohol. Diphenyl ether [2] swells partially hydrated acetate to a voluminous mass which may then be brought into solution by the addition of a small amount of acetone, acetylene tetrachloride or alcohol. Diphenyl ether (phenyl oxide) is an extremely stable body, of a geranium-like odor, and boiling at 252°. It induces temporary or partial plasticity with hydrated acetylcellulose, and has a low volatility. Benzyl methyl-, benzyl ethyl-, benzyl phenyl-, and dibenzyl-ethers, which boil respectively at 167°, 182°, 286° and 295°, all gelatinize or dissolve acetated cellulose when warmed with alcohol. Ethers of benzyl with the dihydroxybenzenes, such as benzylquinol, dibenzylquinol, dibenzylresorcinol, and dibenzylcatechol, all solids with melting points of 122°, 130°, 76°, and 61°, gelatinize acetated cellulose in the cold. Pyrocatechin diethyl ether has been patented by H. Dreyfus as an acetate solvent. With guaiacol (catechol mono-methyl ether) acetone-soluble cellulose acetate entirely dissolves in the cold, forming a viscous solution of a faint, agreeable creosote-like odor. Such solutions may be thinned with mixtures of alcohol, acetone or benzene and produce excellent lacquers. The boiling point

1. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264, 1911; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

2. E.P. 8945, 1909; abst. J.S.C.I. 1909, **28**, 1271. F.P. 402083, 1909; abst. J.S.C.I. 1909, **28**, 1270; Mon. Sci. 1910, (4), **73**, 168.

(200°) causes slow setting and hardening of the cellulose acetate in lacquers, for which purpose it should be used in quantities of about 2 to 4 times the weight of cellulose acetate Catechol dimethyl ether (veratrol) is too expensive for commercial use.

Aldehydes. Formaldehyde has been proposed for a plastic compound in conjunction with cellulose acetate and glue,[1] paraformaldehyde with shellac, aniline and acetylcellulose, while L. Collardon produces phenol-aldehyde condensation products from formaldehyde or other methylene-containing compounds,[2] and unites acetylcellulose with the condensate while the latter is in the primary or soluble stage.[3] One of the most important solvents of aldehydic constitution for cellulose esters is undoubtedly trichloraldehyde, either as chloral hydrate or chloral alcoholate. W. Parkin and A. Williams[4] renders acetylcellulose plastic by the admixture therewith of various amounts of chloral alcoholate, the amount of the latter to be added depending upon the degree of plasticity and flexibility desired in the finished product. In the L. Lederer process[5] 3 parts of cellulose acetate to 2 parts of chloral hydrate or chloral alcoholate are intimately mixed, and then compressed into the required form by the aid of pressure and gentle heat.[6] Camphor may also be used in connection

1. U.S.P. 952724, 1910; abst. J.S.C.I. 1910, **29**, 503. E.P. 4154, 1909; abst. J.S.C.I. 1910, **29**, 100. F.P. 402028, 1909; abst. J.S.C.I. 1909, **28**, 1212. D.R.P. 242467, 1908; abst. Kunst. 1912, **2**, 59; C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **86**, 111.

2. For full description of phenol-aldehyde condensation products, with eleven hundred literature and patent citations, see Part Five.

3. E.P. 1598, 1912; abst. Kunst. 1913, **3**, 276. Butyl chloral hydrate is also solvent.

4. E.P. 26657, 1909; abst. J.S.C.I. 1910, **29**, 1152. F.P. 421 010, 1910; abst. J.S.C.I. 1911, **30**, 416.

5. E.P. 9537, 1907; abst. J.S.C.I. 1908, **27**, 589. F.P. 377010, 1907; abst. J.S.C.I. 1907, **26**, 1027; Mon. Sci. 1908, (4), **68**, 444. D.R.P. 189703, 1902; abst. Chem. Zts. 1907, **6**, 387; Chem. Zentr. 1907, II, 1822; Chem. Tech. Rep. 1907, **31**, 570; Wagn. Jahr. 1907, II, 562; Mon. Sci. 1910, (4), **73**, 159. D.R.P. 152111, 1902; abst. Zts. ang. Chem. 1904, **17**, 1250; Chem. Centr. 1904, II, 382; Mon. Sci. 1910, (4), **73**, 159; Jahr. Chem. 1904, 1168. D.R.P. 220228, 1907; abst. Chem. Zts. 1910, **9**, 1934; Chem. Ind. 1910, **33**, 271; Chem. Tech. Rep. 1910, **34**. 180; Wagn. Jahr. 1910, II, 589. Aust. P. 34908, 1908; Zts. ang. Chem. 1909, **22**, 505.

6. The two German patents cover same claims as each of the

with the chloral derivative. A. Eichengruen uses phenol, chloral and acetylcellulose,[1] obtaining particularly favorable results when the volatile solvent portion consists of tetrachlorethane, with or without alcohol.[2] C. Ellis[3] claims to have discovered that by uniting chloral with various complex organic bodies containing hydroxyl groups, compositions are obtained which have a softening or solvent action upon nitrocellulose and acetylcellulose, and are less inflammable than camphor or waxy bodies which have heretofore been employed in the celluloid art. Of the hydroxylated organic bodies, amyl lactate is stated as particularly suitable. Castor oil when treated with chloral is said to yield products which are especially useful. When ordinary castor oil is mixed with about an equal weight of chloral, the mixture heated gently to produce the chloral derivative, and the excess of chloral removed by washing or distillation, the new compound is mixed with acetylcellulose in varied amounts depending upon the hardness desired in the finished product.

In the manufacture of formaldehyde from wood alcohol, certain by-products necessarily arise, which are marketed under trade names such as Solvent L., P-2, and Formace, and which contain methyl acetate, acetaldehyde, acetone and other bodies of variable and undetermined compositions. These liquids are lighter than water, will usually mix with benzine and benzene in any proportion without turbidity, are somewhat hygroscopic, and partially dissolve in water. They dissolve acetone-soluble cellulose acetate with avidity, and in combination with solvents of lower volatility and higher boiling point like tetrachlorethane, produce compound solvents

French and English, i. e., F.P. and E.P. claim the use of chloral hydrate and chloral alcoholate as substitutes for camphor with cellulose acetates, while D.R.P. 189703 claims chloral alcoholate, and D.R.P. 220228 claims chloral hydrate. D.R.P. 189703 gives 3 parts cellulose acetate and 2 parts chloral ethyl alcoholate dissolved together at a low temperature. D.R.P. 220228 gives chloral hydrate with ethyl acetate or tetrachlorethane.

1. E.P. 27258, 1910; abst. J.S.C.I. 1911, **30**, 1112. F.P. 419 530, 1910; abst. J.S.C.I. 1911, **30**, 205.

2. First Add. 13237, dated Sept. 29, 1911, to F.P. 419530; abst. J.S.C.I. 1911, **30**, 415.

3. U.S.P. 999490, 1911; abst. J.S.C.I. 1911, **30**, 1051.

which are efficient and at the same time reasonable in cost. For instance, Solvent L. consists of about 85% methyl acetate and 15% acetone by volume, while P-2 Solvent contains ethers 45%, esters 35%, and aldehydes 20%, is water-white and neutral. Both are miscible in any proportion with chloroform, ether, acetone, tetrachlorethane or benzene.

Ketones. Acetone (dimethyl ketone) is usually obtained by the dry distillation of commercial acetate of lime, which consists of calcium acetate and small amounts of the calcium salts of propionic and homologous acids. In the process of J. Becker[1] the calcium salts are made absolutely neutral, and the formation of free lime is prevented during the process by the introduction of a stream of carbon dioxide or gas rich in carbon dioxide. In another recent method[2] in which it is claimed that acetone may be obtained in higher yield than by any other known method, a reducing agent or amine is allowed to act upon a monobasic acid or ester.[3] In order to avoid the agglomeration of the hot mass which is apt to occur when calcium or barium acetate is heated, a double acetate is substituted instead, whereby when the double acetate—as of barium and calcium—is raised to the required temperature, a spongy mass of the double carbonate is formed, which is so efficient as a thermal conductor as to render mechanical heat unnecessary.[4]

1. D.R.P. 170533, 1903; abst. J.S.C.I. 1907, **26**, 279; Zts. ang. Chem. 1907, **20**, 206; Chem. Zentr. 1906, I, 1807; Wagn. Jahr. 1906, II, 19; Chem. Zts. 1907, **6**, 88.

2. P. de la Fresnaye and E. Cadoret de la Gabiniere, F.P. 451374, 1912; abst. J.S.C.I. 1913, **32**, 625; C.A. 1913, **7**, 3227.

3. The following example is given: 700 parts of 40 per cent. acetic acid are mixed with 230 parts of sodium chloride, 210 parts of metallic iron, and 150 parts of methyl or ethyl alcohol, and 275 parts of sulfuric acid are slowly added; when esterification is complete, 100 parts of potassium permanganate and 185 parts of cupric chloride are added, the mixture is allowed to stand for 48 hours, and the acetone distilled off.

4. Cadoret de la Gabiniere and E. Deligeon, F.P. 439732, 1911; abst. J.S.C.I. 1912, **31**, 711. For a fermentation process for producing acetone and higher alcohols from starch, sugar and other carbohydrates, see A. Fernbach and E. Strange, F.P. 448364, 1912; abst. J.S.C.I. 1913, **32**, 377. E.P. 15203, 15204, 16295, 1911; abst. J.S.C.I. 1912, **31**, 1091, 1143. See also L. Pages, E. Camus, R. Buchemin and Soc. Pages Camus et Cie, E.P. 13508, 1907; abst. J.S.C.I. 1907, **26**, 958. E.P. 8757, 1906; abst. J.S.C.I. 1906, **25**,

Acetone boils at 56.5°, and has sp. gr. of 0.79115 at 19.4/4°,[1] 0.78645 at 25/4,°[2] and 0.77474 at 35/4°. It is miscible with water, alcohol, ether, chloroform, acetylene tetrachloride and ethyl or amyl acetates in all proportions without turbidity, and also with benzine and benzene when sufficiently free from water. Acetone is of first importance as an acetylcellulose solvent, because it completely dissolves that partially hydrated acetic ester which gives films of greatest strength and tenuity, and hence the ester commercially most valuable. Normal triacetylcellulose is insoluble in acetone. As hydration of the normal triacetate proceeds, a point is reached when the ester is soluble in 99.5% acetone. If hydration is allowed to continue from this point, the acetated cellulose becomes soluble in acetone containing increasing amounts of water, until products soluble in pure water result. And as the percentage of water in the acetone increases, so do the desirable properties of the acetate correspondingly decrease. Acetone as a cellulose acetate solvent has been repeatedly described in patent literature,[3]

634. F.P. 361379, 1905; abst. J.S.C.I. 1905, **24**, 687. See Add. of July 27, 1906, to F.P. 361379; abst. J.S.C.I. 1907, **26**, 43.

1. F. Eisenlohr, Zts. Phys. Chem. 1910, **75**, 585; abst. Bull. Soc. Chim. 1911, (4), **10**, 1221; Chem. Zentr. 1911, I, 625; J.C.S. 1911, **100**, ii, 81; C.A. 1911, **5**, 1218.

2. Hubbard, Zts. Phys. Chem. 1910, **74**, 217; abst. Bull. Soc. Chim, 1911, (4), **10**, 831; J.C.S. 1910, **98**, ii, 809; C.A. 1911, **5**, 2401. "Koline" is a mixed solvent, apparently consisting of acetone and denatured ethyl alcohol.

3. E.P. 24067, 1906; abst. J.S.C.I. 1907, **26**, 1213. F.P. 371447, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 79; Chem. Tech Rep. 1907, **31**, 149. U.S.P. 838350, 1906; abst. J.S.C.I. 1907, **26**, 165; Mon. Sci. 1907, (4), **66**, 1161. Reissue 12637 thereon dated April 23, 1907; abst. J.S.C.I. 1907, **26**, 634; Mon. Sci. 1907, (4), **66**, 159. E.P. 19330, 1905, Void; abst. J.S.C.I. 1906, **25**, 865. F.P. 358079, 1905; abst. Mon. Sci. 1906, (4), **64**, 169; J.S.C.I. 1906, **25**, 195. Hung. P. 35866, 1905. Belg. P. 187308, 1905. Aust. P. 41461, 1909. Can. P. 103045. It. P. No. 97, Vol. 215, 1905. D.R.P. Anm. M. 28289, 1905. F.P. 427265, 1911; abst. J.S.C.I. 1911, **30**, 1051. Chem. Tech. Rep. 1911, **35**, 481. Hung. Appl. O.-674, 1912. Aust. P. 29b. A. 1787, 1912; abst. Kunst. 1912, **2**, 460. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, (4), **60**, 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**,

either alone or in combination with acetylene tetrachloride,[1] camphor,[2] or pentachlorethane.[3] A. Zimmer[4] treats starched linen with cellulose acetate in acetone. Nitrocellulose and acetylcellulose are often combined by means of this mutual solvent. Acetone and chlorinated stearic acid has been used for phonograph cylinders.[5] The ready miscibility of acetone

870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, (4), **60**, 54. Aust. P. 31391. It. P. 62042, 1901. U.S.P. 987692, 1911; abst. J.S.C.I. 1911, **30**, 485; Chem. Tech. Rep. 1911, **35**, 250. E.P. 14271, 1910; abst. J.S.C.I. 1911, **30**, 485. F.P. 417274, 1910; abst. J.S.C.I. 1911, **30**, 485. Aust. P. of Aug. 14, 1909; July 21, 1910. D.R.P. 222450, 1908; abst. J.S.C.I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Wagn. Jahr. 1910, **56**, II, 434; Chem. Zentr. 1910, **81**, 48; Chem. Zts. 1910, **9**, 1902; C.A. 1910, **4**, 2875. E.P. 4863, 1903; abst. J.S.C.I. 1904, **23**, 382. F.P. 324121, 1902; abst. J.S.C.I. 1904, **23**, 569. F.P. 432046, 1911; abst. J.S.C.I. 1912, **31**, 24. First Add. dated July 7, 1911, to F. P. 432046; abst. J.S.C.I. 1912, **31**, 225. Second Add. to F.P. 432046, abst. J.S.C.I. 1912, **31**, 225. Third Add. 15933, dated Jan. 4, 1912, to F.P. 432046; abst. Chem. Ztg. 1912, **34**, 1174. Fourth Add. 15894, dated April 4, 1912; abst. J.S.C.I. 1912, **31**, 1119. Fifth Add. 16316, dated April 1, 1912; abst. J.S.C.I. 1912, **31**, 1119. Sixth Add. dated Aug. 5, 1912, to F.P. 432046, abst. J.S.C.I. 1913, **32**, 283. Seventh Add. dated Sept. 16, 1912, to F.P. 432046; abst. J.S.C.I. 1913, **32**, 420. E.P. 20978, 1911, same as First Add. to F.P. 432046; abst. Kunst. 1913, **3**, 195. E.P. 20852, 1912. E.P. 21376, 1912, division of 20978, 1911; abst. J.S.C.I. 1913, **32**, 133. E.P. 20977, 1911, same as F. Appl. July 5, 1911; abst. J.S.C.I. 1913, **32**, 133; C.A. 1913, **7**, 891. Belg. P. 241250, 246250, 246251, 1912. Aust. P. 12o, Mar. 16, 1910; Mar. 9, 1911.

1. E.P. 11625, 1909; abst. J.S.C.I. 1909, **28**, 1030. F.P. 402072, 1909; abst. J.S.C.I. 1909, **28**, 1221. D.R.P. 240751, 1908; abst. C.A. 1912, **6**, 2179; Wagn. Jahr. 1911, II, 421; Kunst. 1912, **2**, 15; Chem. Ind. 1911, **34**, 798; Chem. Ztg. 1911, **35**, 624; Zts. ang. Chem. 1912, **25**, 47; Chem. Zentr. 1911, **82**, 1843; D. R. P. 248559, 1909; Add. to D.R.P. 240751; abst. Wagn.Jahr. 1912, II, 445; Kunst. 1912, **2**, 296; Zts. ang. Chem. 1912, **25**, 1884; C.A. 1912, **6**, 2849; Chem. Tech. Rep. 1912, **36**, 437; Zts. ang. Chem. 1912, **25**, 1884; Chem. Zentr. 1912, **83**, 305.

2. E.P. 19735, 1908; abst. J.S.C.I. 1910, **29**, 18; F.P. 393963, 1908; abst. J.S.C.I. 1909, **28**, 257. D.R.P. 223793, 1907, being Add. to D.R.P. 210519; Mon. Sci. 1913, **78**, 38; Wagn. Jahr. 1909, II, 555; 1910, II, 483. Aust. P. 51094, 1908.

3. E.P. 14364, 1910; abst. J.S.C.I. 1910, **29**, 1152. D.R.P. Anm. F. 28111 of Aug. 25, 1909; refused Feb. 20, 1911. Aust. P. 46991, 1910; Swiss P. 52438; abst. Kunst. 1912, **2**, 135. F. P. 417250, 1910; abst. J.S.C.I. 1911, **30**, 19.

4. U.S.P. 1025731, 1912; abst. C.A. 1912, **6**, 1994. E.P. 12406, 1910; abst. J.S.C.I. 1911, **30**, 206. D.R.P. 242786, 1910; abst. C.A. 1912, **6**, 2182; Chem. Tech. Rep. 1912, **36**, 79; Zts. ang. Chem. 1912, **25**, 512.

5. U.S.P. 855556, 1907.

with water, low boiling point and hygroscopicity, are the main disadvantages found in its use. However, it is seldom, if ever, used as a cellulose ester solvent alone, being usually combined with higher boiling solvents as tetrachlorethane. By the catalytic hydrogenation of acetone in presence of nickel at temperatures above 200°, the main product formed is isobutyl ketone with smaller amounts of di-isobutyl ketone (valerone).[1] The mixture in conjunction with acetone produces an excellent solvent for those forms of acetylcellulose which dissolve in pure acetone. In addition to the rather tedious bisulfite process, acetone may be purified by the method of K. Shipsey and E. Werner,[2] who have found that sodium iodide can unite with acetone to form a crystalline compound having the composition $NaI,3C_3H_6O$. They show that acetone of a high degree of purity may be prepared from the commercial article in a simple manner by the aid of sodium iodide, the hydrated salt $NaI,2H_2O$ being preferable on account of its ready solubility in acetone. The solution when cooled to about 8° gives an excellent yield, and it is possible to obtain 70° of the acetone in a pure state in a single operation. In the manufacture of acetone from acetate of lime by dry distillation, after the acetone proper has all been distilled, the next fraction, arbitrarily taken between the limits of 65-125° is known as light acetone oil.[3] The fraction beyond this is termed "heavy acetone oil." Light acetone oil in its crude state is

1. A. Lassieur, Compt. rend. 1913, **156**, 795; abst. J.S.C.I. 1913, **32**, 379; C.A. 1913, **7**, 2214; J.C.S. 1913, **104**, i, 444.

2. Chem. Soc. Proc. 1913, **29**, 194; abst. J.S.C.I. 1913, **32**, 611.

3. For the manufacture of acetone oil from wool combing washings, see P. Baechlin, Rev. Chim. Ind. 1902, **15**, 240; abst. J.S.C.I. 1902, **21**, 1271. For manufacture of acetone, see Pages Camus et Cie, F.P. 361379, 1905. First Add. July 7, 1906. Second Add. Mar. 8, 1907. Third Add. Oct. 10, 1907. E.P. 8757, 1906. U.S.P. 933107, 1909; abst. J.S.C.I. 1906, **25**, 634, 687; 1907, **26**, 43, 1002; 1908, **27**, 277; 1909, **28**, 1029; C.A. 1907, **1**, 2322; 1910, **4**, 85. G. Pereire and G. Guignard, F.P. 316060, 316061, 1901; abst. J.S.C.I. 1902, **21**, 541, 1096. For the manufacture of methylene acetone and homologues, see D.R.P. 242612, 1910; abst. C.A. 1913, **7**, 2291; Zts. ang. Chem. 1912, **25**, 333; Chem. Zentr. 1912, I, 385; Chem. Tech. Rep. 1912, **36**, 107; Wagn. Jahr. 1912, II, 57; Chem. Zts. 1912, II, No. 2700. For sp. gr. of ethyl methyl, dimethyl, methylisopropyl, methylpropyl and ethylpropyl ketones, see Eisenlohr, Zts. phys. Chem. 1910, **75**, 585.

a light amber liquid of penetrating and disagreeable odor, sp. gr. 0.829 at 22°, and soluble 10-25% in water, the solubility depending upon the proportion of lower water-soluble ketones therein. It consists essentially of ethyl-methyl ketone and diethyl ketone. The former—called methyl acetone—is an agreeable smelling liquid boiling at 81°, is superior to acetone as a cellulose acetate solvent, and in addition is not so volatile and less hygroscopic. Methyl-propyl ketone (ethyl acetone) boiling at 102°, is but slightly soluble in water, methyl-*iso*-propyl ketone (dimethyl-*l*-acetone, amylene oxide) boils at 102°, and dissolves acetone-soluble acetylcellulose readily. Furthermore, the lower boiling petroleum benzines may be added to purified light acetone oils, thus introducing a water-insoluble, non-hygroscopic and inexpensive acetylcellulose non-solvent without change in the boiling point and speed of evaporation of the mixture. The quality of light acetone oil is determined by the odor, specific gravity, fractionation, and relative solubility in water.[1] Acetone oil may also be obtained from wool washings,[2] and has been used to preserve wood by impregnation.[3]

C. Piest has described an acetone substitute which readily dissolves cellulose acetate.[4] It is a clear, colorless, neutral liquid of sp. gr. 0.915 at 15° and distilling 51-75°. It apparently is a by-product from the acetone manufacture. Such a product is for sale in the United States under the name "Ketone Solvent," consisting approximately of 65% ethers, 28% aldehydes and 7% esters, boils between 60-75°, miscible with 2 volumes of benzene without turbidity and has a sp. gr. of about 0.9. It dissolves readily both cellulose nitrates and acetates, and as a solvent for the latter is preferably used in conjunction with a higher boiling and less hygroscopic solvent such as tetra-

1. Kunst. 1912, **2**, 256.
2. Bull. Assoc. Chim. Sucr. Dist. 1901, (6), **19**, 662; abst. J.S.C.I. 1898, **17**, 266, 485; 1899, **18**, 292, 405; 1902, **21**, 164.
3. Hontsch & Co., D.R.P. 239697, 1910; Add. to D.R.P. 237150; abst. C.A. 1912, **6**, 2160; Zts. ang. Chem. 1911, **24**, 2288; Wagn. Jahr. 1911, II, 563; Chem. Tech. Rep. 1911, **35**, 568. D.R.P. 237150; abst. C.A. 1912, **6**, 1977; Wagn. Jahr. 1911, II, 563; Chem. Tech. Rep. 1911, **35**, 455; Zts. ang. Chem. 1911, **24**, 1664.
4. Chem. Ztg. 1913, **37**, 299; abst. C.A. 1913, **8**, 2116.

chlorethane. Dichloracetone,[1] benzyldihydrocarvone, *a*-naphthyldihydrocarvone, benzyldihydropulegon, benzyl-magnesium halogen and naphthyl-magnesium halogen,[2] have been patented as acetylcellulose solvents for plastic formation. The interaction of organo-magnesium compounds upon such hydroaromatic unsaturated ketones as carvone, pulegone and cyclohexanone, leads to the production of useful solvents and softeners. The proper proportion of benzyldihydrocarvone is stated to be 55% on the weight of acetylcellulose, acetone and alcohol being the preferable solvent. Acetophenone (methylphenyl ketone, hypnone) boils at 210°, and is a useful solvent[3] and softener.[4] In combination with acetylene tetrachloride[5] it is claimed to be especially valuable. Acetylmethyl alcohol (acetol), and salicyl-acetol (salacetol, salantol), have also been described as useful. Benzophenone, chlorinated acetophenone, and methyl acetone[6] are all useful acetylcellulose solvents, especially when warmed with a small amount of alcohol or acetone. According to W. Beatty[7] useful compositions are formed by ketone condensation products

1. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **31**, 652. Belg. P. 241251.

2. D.R.P. 202720, 1907; abst. J.S.C.I. 1908, **27**, 1220; Zts. ang. Chem. 1908, **21**, 2428; Chem. Zentr. 1908, II, 1837; Jahr. Chem. 1905-08, II, 993; Mon. Sci. 1912, **77**, 57.

3. U.S.P. 1005454, 1911; abst. J.S.C.I. 1911, **30**, 1249. E.P. 476, 1910; abst. J.S.C.I. 1910, **29**, 1082. F.P. 411298, 1910; abst. J.S.C.I. 1910, **29**, 978; Phot. Ind. 1910, 1221; Eders Jahr. 1911, 526. Aust P. 50656, 1910; abst. Kunst. 1912, **2**, 77; Phot. Ind. 1911, 28; Eders Jahr. 1911, 526. Belg. P. 222106, 1910. Hung. Anm. M. 3691, Dec. 30, 1909. Swiss. P. 51839, 1910; abst. Kunst. 1912, **2**, 77.

4. U.S.P. 774677, 1904; abst. J.S.C.I. 1904, **23**, 1159. E.P. 7088, 1902; abst. J.S.C.I. 1903, **22**, 563. F.P. 319724, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Add. 811 dated Mar. 18, 1902, to F.P. 319724; abst. J.S.C.I. 1903, **22**, 563. D.R.P. 145106, 1902; abst. Jahr. Chem. 1904, 1168; Mon. Sci. 1904 (4), **60**, 93; Zts. ang. Chem. 1903, **16**, 1090; Chem. Centr. 1903, II, 1155. D.R.P. 151918, 1902. Add. to D.R.P. 145106; abst. Chem. Centr. 1904, II, 1180; Jahr. Chem. 1904, 1168. D.R.P. 152111, 1902.

5. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251.

6. U.S.P. 999490, 1911; abst. J.S.C.I. 1911, **30**, 1051.

7. F.P. 447645, 1912; abst. J.S.C.I. 1913, **32**, 283; C.A. 1913, **7**, 2115; Kunst. 1913, **3**, 116. Belg. P. 252594; abst. Kunst. 1913, **3**, 276. Can. P. 147578, 147579, 1913; abst. C.A. 1913, **7**, 2127, 2128.

with a phenol, or a hydroxy derivative of an aromatic hydrocarbon, e. g. dihydroxydiphenyldimethylmethane, with or without a solvent such as acetone or chloroform. For instance, 50 parts of acetylcellulose and 40 parts of dihydroxydiphenyldimethyl methane may be incorporated with a sufficient quantity of a suitable solvent to form a plastic mass.

Mesityl oxide, a colorless liquid boiling at 129.5°, is a ready solvent of nitro-cellulose, but not of partially hydrated acetylcellulose. It is a constituent of the acetone oils. It is to be noted that heavy acetone oil does not dissolve acetone-soluble acetylcellulose, while light acetone oil does. It is probably a true generalization, that while ascending the scale in molecular weight of the paraffin ketones, the solvent power for nitrocellulose is nearly stationary, but rapidly decreases to insolubility for acetylcelluloses.

Acids. The simplest organic acid—formic—is a solvent of certain cellulose formates and acetates, as claimed in the patented processes of Bemberg[1] and Donnersmarck.[2] As a solvent for starch,[3] it is inferior to acetic acid, although E. Blumer[4] has obtained protection for a method of preparing starch soluble in formic acid. Formic acid is seldom, if ever, used as a solvent.

Cellulose monoacetate and diacetate are difficultly and incompletely soluble in acetic acid, and in the process of acetation, complete solubility of the acetated cellulose in the esterizing mixture does not occur until substantially all of the

1. E.P. 2511, 1907; abst. J.S.C.I. 1907, **26**, 634. Jour. Soc. Dyers and Col., 1907, **23**, 215. F.P. 376262, 1907; abst. J.S.C.I. 1907, **26**, 988. Mon. Sci. 1908, (4), **68**, 87. D.R.P. 189836, 189837, 1908; abst. Zts. ang. Chem. 1908, **21**, 268; Jahr. Chem. 1905-08, 983; J.C.S. 1908, **94**, i, 321; Chem. Ind. 1907, **30**, 617.

2. U.S.P. 922340, 1909; abst. J.S.C.I. 1909, **28**, 671. F.P. 400652, 1909; abst. J.S.C.I. 1909, **28**, 1061. D.R.P. 237718, 1907. It. P. 303-136-101262, 1909.

3. U.S.P. 778173, 1904; abst. J.S.C.I. 1905, **24**, 98. E.P. 9868, 1902; abst. J.S.C.I. 1903, **22**, 1008; Mon. Sci. 1904, (4), **60**, 37. F.P. 334154, 1903; abst. J.S.C.I. 1904, **23**, 29. D.R.P. 182558, 1903; abst. Zts. ang. Chem. 1907, **20**, 1781; Mon. Sci. 1909, (4), **70**, 77. Belg. P. 171743, 1903.

4. D.R.P. 137330, 1901; abst. Chem. Centr. 1903, I, 306; Jahr. Chem. 1903, 1005; Zts. ang. Chem. 1903, **16**, 90. F.P. 322206, 1902; abst. J.S.C.I. 1903, **22**, 310. E.P. 19872, 1902; abst. J.S.C.I. 1903, **22**, 642.

cellulose has been transformed into triacetate. Dry triacetylcellulose is soluble in glacial acetic acid only with great difficulty. It may, however, be dissolved by grinding the acetate with sand, passing through an 80-mesh sieve, and heating the powder on a water bath with the acetic acid for several hours with frequent agitation. Acetic acid, of course, is the solvent for any cellulose acetate which passed into solution in the acetating mixture. It has occasionally been used as a solvent for the cellulose formates, as in the invention of J. Bemberg.[1] For stiffening incandescent mantles, acetic acid solutions of acetylcellulose have been employed to a limited extent. Oleic acid has been used in conjunction with the cellulose acetates in the manufacture of artificial silk more to induce pliability,[2] and as a general softening agent.[3] It has no solvent action. Ricinoleic acid has been recommended for the same purpose. Sulfonated fatty acids [4] and chlorinated stearic acids [5] are used only for imparting the mechanical effect of pliancy.

Lactic acid in the hands of C. Waite,[6] the Vereinigte Glanzstoff Fabriken [7] and A. Schloss [8] has proven a valuable

1. E.P. 2511, 1907; abst. J.S.C.I. 1907, **26**, 634. Jour. Soc. Dyers and Col. 1907, **23**, 215. F.P. 376262, 1907; abst. J.S.C.I. 1907, **26**, 988; Mon. Sci. 1908, (4), **68**, 87. D.R.P. 189836, 189837, 1908; abst. Zts. ang. Chem. 1908, **21**, 268; Jahr. Chem. 1905-08, 983; J.C.S. 1908, **94**, i, 321; Chem. Ind. 1907, **30**, 617.

2. U.S.P. 792149, 1905; abst. J.S.C.I. 1905, **24**, 799; Mon. Sci. 1906, (4), **64**, 22.

3. U.S.P. 712200, 1902; abst. Mon. Sci. 1903, (4), **60**, 165.

4. E.P. 14142, 1911; abst. J.S.C.I. 1912, **31**, 680; C.A. 1913, **7**, 217. Aust. P. 55527; abst. Kunst. 1913, **3**, 38.

5. U.S.P. 855556, 1907. U.S.P. 953454, 962877, 1910; abst. J.S.C.I. 1910, **29**, 940.

6. U.S.P. 690211, 1901; abst. J.S.C.I. 1902, **21**, 272.

7. U.S.P. 1029341, 1912; abst. J.S.C.I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164. E.P. 8313, 1911; abst. J.S.C.I. 1911, **30**, 1050; Chem. Tech. Rep. 1911, **35**, 556; 1912, **36**, 532; C.A. 1912, **6**, 3018. F.P. 428069, 1911; abst. J.S.C.I. 1911, **30**, 1156. Aust. App. 2994, 1911.

8. U.S.P. 922340, 1909; abst. J.S.C.I. 1909, **28**, 671. E.P. 6554, 1909; abst. J.S.C.I. 1910, **29**, 18. D.R.P. 239701, 1910; abst. Chem. Zentr. 1911, **82**, 1502; C.A. 1912, **6**, 2169; Chem. Tech. Rep. 1911, **35**, 556. D.R.P. 237599, 1907; abst. C.A. 1912, **6**, 1679; Zts. ong. Chem. 1911, **24**, 1838; Wagn. Jahr. 1911, II, 419; Chem. Zentr. 1911, **82**, 814. Chem. Tech. Rep. 1911, **35**, 481. Belg. P. 214671, 1909. F.P. 400652, 1909; abst. J.S.C.I. 1909, **28**, 1061; Mon. Sci. 1910, (4), **73**, 165. D.R.P. 237718, 1907; abst. Zts. ang. Chem. 1911, **24**, 1988; Chem. Zentr. 1911, II, 922; Wagn. Jahr. 1911, II, 418; Chem. Ind. 1911, **34**, 573; Chem. Tech. Rep. 1911, **35**, 481.

direct solvent and plastic inducing body for both acetylated and formylated cellulose. The disadvantages of lactic acid are its solubility in water and pronounced tendency to absorb moisture. Cellulose acetate may readily be combined with lactic acid in the cold [1] to a mouldable composition. Oxalic malic, citric, tartaric and lactic acids have been proposed as hydrating agents, but for practical purposes water is equally as efficient and less expensive.[2] Propionic, butyric and valerianic acids in conjunction with alcohol are solvents of partially hydrated cellulose acetate. Salicylous acid is a solvent when heated, and in the cold upon the addition of ethyl alcohol. The solvent effect of salicylous acid is best brought out by dissolving the acetone-soluble modification in it by heat. Upon cooling the product sets to a jelly, but the addition of alcohol to the solution, gives a permanently clear liquid.

Esters.. Triphenyl-, tricresyl-, and trinaphthyl-phosphates,[3] their halogen substitution products;[4] triphenyl-, tricresyl- and trinaphthyl-thiophosphates,[5] diphenyl-, dicresyl-, and dinaphthyl-phosphoric acid anilids, or phenyl-, cresyl- or naphthyl-phosphoric acids;[6] tetranitrodinaphthyl-, and monochlortriphenyl-phosphate;[7] or tricresyldinitrotri-

C.A. 1912, **6**, 1672. It. P. 303-136-101262, 1909.

1. F.P. 421854, 1909; abst. J.S.C.I. 1911, **30**, 416.

2. E.P. 24067, 1906; abst. J.S.C.I. 1907, **26**, 1213. F.P. 371447, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **60**, 79; Chem. Tech. Rep. 1907, **31**, 149.

3. Zuehl and Eisenmann, D.R.P. 128120, 1901; abst. Zts. ang. Chem. 1902, **15**, 113; Chem. Zentr. 1902, I, 387; Wagn. Jahr. 1902, 593; Chem. Zts. 1901-2, **1**, 600; Russ. P. 7848, 1903. Pharm. Centralh. 1902, **43**, 115. E. Zuehl, E.P. 8072, 1901; 23445, 1902. F.P. 309962, 1901; abst. J.S.C.I. 1902, **21**, 65, 719, 1467. A. Maschke (D.R.P. 267407, 1913; abst. J.S.C.I. 1914, **33**, 138; Kunst. 1914, **4**, 14) employs triphenyl-, phenylcresyl- and tricresyl-phosphate for the impregnation of roofing paper.

4. Zuehl and Eisenmann, D.R.P. 142832, 1901; abst. Zts. ang Chem. 1903, **16**, 683; Chem. Zentr. 1903, II, 171; Wagn. Jahr. 1903, 569; Chem. Zts. 1903-4, **3**, 261. The products specified are the neutral phosphates of dichlorphenol, tetrachlorphenol, dichlorcresol, dichlornaphthol and tetrachlornaphthol.

5. Ibid. D.R.P. 140164, 1901; abst. Zts. ang. Chem. 1903, **16**, 286; Chem. Zentr. 1903, II, 860; Wagn. Jahr. 1903, II, 569. Russ. P. 8893, 1904.

6. Ibid. D.R.P. 144648, 1902; Add. to D.R.P. 128120, 1901; abst. Zts. ang. Chem. 1903, **16**, 1064; Chem. Zentr. 1903, II, 1041; Wagn. Jahr. 1903, II, 570; Chem. Zts. 1903-4, **3**, 261.

7. Ibid. D.R.P. 142971, 1902; abst. Zts. ang. Chem. 1903, **16**,

naphthyl- and dichlordiphenyl-thiophosphate,[1] have been used for some years as nitrocellulose solvents and plastic-inducing bodies. They have also been found excellent cellulose acetate solvents. Triphenyl phosphate consists of slightly deliquescent colorless needles, insoluble in water, soluble in alcohol, and very soluble in acetone, ether or chloroform. Of the cresyl phosphates, tri-*o*-tolyl phosphate is an oil, insoluble in water, soluble in alcohol, ether and acetone, while tri-*p*-tolyl phosphate is colorless tables, melting at 78° and dissolving readily in acetone. Both tri-*a*-naphthyl and tri-*b*-naphthyl-phosphates are solids which dissolve readily in acetone, less soluble in acetylene tetrachloride. W. Lindsay [2] has found that plastic acetylcellulose compounds result which are substitutes for celluloid, when triphenyl phosphate, either in solid form or dissolved in acetone, is added to acetylcellulose, either with or without a small amount of urea [3] to increase the stability. The triphenyl phosphate appears to increase both the strength and tenacity, and to still further reduce the inflammability. Acetylcellulose will dissolve in the presence of triphenyl phosphate in either acetone, ethyl acetate, chloroform, pyridine or acetylene tetrachloride. From 10-20% of the weight of acetyl-

683; Chem. Zentr. 1903, II, 171; Wagn. Jahr. 1903, 569; Chem. Zts. 1903-4, **3**, 261. E.P. 4383, 1902. They have also patented (D.R.P. 139589, 1900; abst. Chem. Zentr. 1903, I, 749; Zts. ang. Chem. 1903, **16**, 286; Wagn. Jahr. 1903, 569; Chem. Zts. 1902-3, **2**, 672. Russ. P. 8855, 1904) carbonic esters of phenols, cresols and naphthols (diphenyl carbonate, dicresyl carbonate, and dinaphthyl carbonate); methyl- and benzyl-oxanilates (D.R.P. 128119, 1901; abst. Zts. ang. Chem. 1902, **15**, 114; Chem. Zentr. 1902, I, 387; Wagn. Jahr. 1902, II, 593). Also mono- or poly-halogen substitution products of aromatic compounds as dichlorbenzol, monochlornaphthalin, in their D.R.P. 128956, 1902; abst. Mon. Sci. 1903, **59**, 4; Zts. ang. Chem. 1902, **15**, 210; Wagn. Jahr. 1902, II, 594.

1. E. Zuehl, E.P. 872, 1901; 4383, 1902; abst. J.S.C.I. 1901, **20**, 74; 1902, **21**, 65.

2. D.R.P. 263056, 1910; Kunst. 1913, **3**, 375. U.S.P. 1045990, 1913; abst. J.S.C.I. 1913, **32**, 19; C.A. 1913, **7**, 699; 1050065, 1913; abst. J.S.C.I. 1913, **32**, 133; Kunst. 1913, **3**, 218. U.S.P. 1067785, 1913; abst. J.S.C.I. 1913, **32**, 823; C.A. 1913, **7**, 3025. E.P. 10794, 1910; abst. J.S.C.I. 1911, **30**, 679. E.P. 10795, 1910; abst. J.S.C.I. 1911, **30**, 205. F.P. 415517, 415518, 1910; abst. J.S.C.I. 1910, **29**, 1299; Mon. Sci. 1912, **77**, 9.

3. U.S.P. 1067785, 1913; abst. J.S.C.I. 1913, **32**, 823; C.A. 1913, **7**, 3025. F.P. 415518, 1910; abst. J.S.C.I. 1910, **29**, 1299; Mon. Sci. 1912, **77**. 9.

cellulose is the usual amount of triphenyl phosphate required to produce a flowable or plastic mass, the addition of 1.5% ether having a tendency to increase the stability and permanency of the mixture. Best films are probably produced when that form of partially hydrated cellulose acetate is used which in solubility is between a chloroform-soluble and acetone-soluble, i. e. in which the hydration has not been carried as far as the acetone-soluble stage. Acetone and triphenyl phosphate will entirely dissolve such an ester. Tricresyl phosphate, diphenylamine, trichlorphenol, and to a lesser extent phenyl salicylate (salol) form plastics as adjuncts to the phosphate. Camphor, in conjunction with triphenyl phosphate in the hands of Lindsay [1] leads to the formation of useful mixtures, the acetylcellulose which is acetone-soluble being first ground with from 15%-30% of camphor and 10-20% triphenyl phosphate to a homogeneous and indistinguishable mixture. From 40%-50% of methyl alcohol is next added, and the mixture left at rest until complete gelatinization occurs, when the mass is ready to be worked or shaped in a similar manner to crude celluloid. While ethyl alcohol and camphor is not a good solvent of cellulose acetate in the cold, methyl alcohol and camphor in certain proportions has a decided dissolving effect. The amount of phosphate used will depend upon the degree of hardness and solidity desired in the finished acetate plastic. The patented process of W. Merckens and H. Manissadjian [10] for the use of phenyl phosphate as acetylcellulose plastic in England was declared void in 1911. In 1910 there was granted to these inventors a series of four separate patents, in which the phosphates and thiophosphates of phenyl, cresyl and naphthyl are combined with acetated cellulose for the formation of plastic masses and the preparation of continuous photographic films.[2]

1. U.S.P. 1041115, 1912; abst. J.S.C.I. 1912, **31**, 1075; C.A. 1912, **6**, 3518; Mon. Sci. 1913, **79**, 110.

2. E.P. 8646, 8647, 1910; abst. J.S.C.I. 1911, **30**, 533, 616; Chem. Tech. Rep. 1911, **35**, 307. F.P. 413657, 413658, 1910; abst. J. S. C. I. 1910, **29**, 1101. F.P. 414679, 414680, 1910; abst. J.S.C.I. 1910, **29**, 1199, 1228. Swiss. P. 51644, 51910; abst. Kunst. 1912, **2**, 77, 99. Belg. P. 223996,1910. Aust. P. 47244; also 53109; abst. Kunst. 1912, **2**, 255. E.P. 6608, 1910; Aust. Anm. 2118, 1910.

Triphenyl borate[1] has been proposed as a softener of difficult inflammability.

An important class of solvents for acetone-soluble acetylcellulose may be obtained by combining monohydric or polyhydric aliphatic or carbocyclic alcohols with monohydric aliphatic acids, specifically acetic acid. Valuable solvents coming under this classfication are the acetic esters of ethyl, ethylene glycol, glycerol, phenyl, benzyl, resorcinol, pyrogallol, and their halogen and nitro-substitution products. Combinations of alcohols with acetic acid produce a series of esters which have a peculiar and energetic solvent action upon cellulose acetates of a wide range of hydration. Methyl acetate is a poor solvent, and inferior to methyl formate. It is a solvent for certain alcohol-soluble acetates, and its solvent action is quickened by the presence of small amounts of acetone or ethyl alcohol. A. Wohl[2] employs methyl acetate as a solvent, and the Societe L'Oyonnithe[3] describe the production of cellulose acetates soluble in this ester.

Ethyl acetate is much superior to the methyl derivative as a solvent, and in general, will dissolve any partially hydrated acetylcellulose which will dissolve in acetone of

1. Farbenfabriken vorm. F. Bayer and Co., U.S.P. 1031616, 1912; J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F. P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29-b, 4624, 10, June 21, 1909.

2. A. Wohl, E.P. 12422, 1910; 3139, 1911; abst. J.S.C.I. 1911, **30**, 888; Chem. Tech. Rep. 1911, **35**, 520. F.P. 425900, 1911; abst. Mon. Sci. 1913, **78**, 121; J.S.C.I. 1911, **30**, 951. Belg. P. 232699, 1911. D.R.Anm. W. 36069, 1910; D.R.P. 246651, 1910; abst. C.A. 1912, **6**, 2529; Chem. Tech. Rep. 1912, **36**, 332; Wagn. Jahr. 1912, II, 445; Zts. ang. Chem. 1912, **25**, 1549; Chem. Zentr. 1912, **83**, 1742. Aust. 29b, A 403, 1911,Mar. 12, 1910; Jan. 14, 1911. D.R.P. 246657, 1910; abst. Kunst. 1912, **2**, 232. F.P.435742, 1912; abst. Mon. Sci. 1913, **78**, 133. The Societe anonyme Le Camphre, F.P. 452432, 1912, combine methyl acetate with tetrachlorethane or acetone as an acetate plastic solvent.

3. Societe L'Oyonnithe, F.P. 427265, 1911; abst. J.S.C.I. 1911, **30**, 1051; Chem. Tech. Rep. 1911, **35**, 481. Hung. Appl. O-674, 1912. Aust. P. 29b, A. 1787, 1912; abst. Kunst. 1912, **2**, 460. F. Klatte (U.S.P. 1084581, 1914; abst. J.S.C.I. 1914, **33**, 219), describes ethers and esters of ethylidene glycol and of vinyl alcohol whose solvent properties for cellulose esters might with profit be investigated.

80%-95% strength. Methods have been published for the formation of cellulose esters both soluble [1] and insoluble [2] in ethyl acetate (so-called acetic ether, or "Star Solvent"). In conjunction with camphor,[3] chloral hydrate,[4] monoacetylethylaniline [5] or ethylbenzoyl-*o*-toluidine,[6] plastic compounds of distinct value may be formed. Some of the cellulose sulfonic acid esters will dissolve in ethyl acetate.[7] Propyl acetate is

1. F.P. 427265, 1911; abst. J.S.C.I. 1911, **30**, 1051; Chem. Tech. Rep. 1911, **35**, 481. Hung. Appl. O-674, 1912. Aust. P. 29b, A. 1787, 1912; abst. Kunst. 1912, **2**, 460. F.P. 375092, 1907; abst. J.S.C.I. 1907, **26**, 877. F.P. 397429, 1908; abst. J.S.C.I. 1909, **28**, 812.

2. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, (4), **60**, 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, (4), **60**, 54. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. Aust. P. 31391. It. P. 62042, 1901.

3. E.P. 19735, 1908; abst. J.S.C.I. 1910, **29**, 18. F.P. 393963, 1908; abst. J.S.C.I. 1909, **28**, 257. D.R.P. 223793, 1907, being Add. to D.R.P. 210519. Aust. P. 51094, 1908.

4. E.P. 9537, 1907; abst. J.S.C.I. 1908, **27**, 589. F.P. 377010, 1907; abst. J.S.C.I. 1907, **26**, 1027; Mon. Sci. 1908, (4), **68**, 444. D.R.P. 189703, 1902; Add. to D.R.P. 152111, 1902; abst. Chem. Zts. 1907, **6**, 387; Chem. Zentr. 1907, **78**, [(5)], 1822; Mon. Sci. 1910, (4), **73**, 159. D.R.P. 152111, 1902; abst. Zts. ang. Chem. 1904, **17**, 1250; Chem. Centr. 1904, II, 382; Mon. Sci. 1910, (4), **73**, 159; Jahr. Chem. 1904, 1168. D.R.P. 220228, 1907; abst. Chem. Zts. 1910, **9**, 1934; Chem. Ind. 1910, **33**, 271. Aust. P. 34908, 1908; abst. Zts. ang. Chem. 1909, **22**, 505.

5. F.P. 427804, 1910; abst. J.S.C.I. 1911, **30**, 1051; Mon. Sci. 1913, **78**, 32; C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 111. German Patent Application C-22897, 1913, Chemische Fabrik von Heyden A. G., describes the use of methyl and ethyl monochloracetates, as cellulose ester solvents.

6. U.S.P. 1031616, 1912; J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 13100, 1900; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4624-10, June 21, 1909.

7. D.R.P. 200334, 1907; abst. J.S.C.I. 1908, **27**, 1130; Mon. Sci. 1911, (5), **74**, 63; Chem. Zts. 1908, **7**, 909; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, 655; Jahr. Chem. 1905-08, 987; J.C.S. 1908, **94**, i. 955; Chem. Ind. 1908, **31**, 499. For the modifying action of ethyl acetate on acetyl chloride in the presence

practically a non-solvent, but propyl chlorstearate, myristate, palmitate and stearate[1] have weak dissolving power, especially in the presence of acetone, alcohol or chloroform and heat. *n*-Butyl acetate is without solvent action. Although cellulose acetates may be prepared which are soluble in amyl acetate, as in the process of Soc. D'Exploitation des Brevets Dolter,[2] such solutions have not the strength requisite for film formation. As a precipitant in the esterizing mixture, amyl acetate is efficient[3] but too costly. Amyl formate[4] is

of cellulose hydrate, see E.P. 11749, 1900; abst. J.S.C.I. 1901, **20**, 741. D.R.P. 163316, 1901; abst. Zts. ang. Chem. 1906, **19**, 204; Chem. Centr. 1905, II, 1301; Mon. Sci. 1906, (4), **64**, 159; Jahr. Chem. 1905-08, II, 984; Chem. Ind. 1905, **28**, 659; Wagn. Jahr. 1905, II, 191. D.R.P. 200916, 1901; being Add. to D.R.P. 163316; abst. Mon. Sci. 1911, (5), **74**, 82; Wagn. Jahr. 1908, II, 364; Zts. ang. Chem. 1908, **21**, 2047; Chem. Zentr. 1908, **79**, 738; Chem. Ind. 1908, **31**, 559. F.P. 319848, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Aust. 42440, 1909.

1. U.S.P. 962877, 1910; abst. J.S.C.I. 1910, **29**, 940.

2. F.P. 375092, 1907; abst. J.S.C.I. 1907, **26**, 877.

3. E.P. 19735, 1908; abst. J.S.C.I. 1910, **29**, 18. F.P. 393963, 1908; abst. J.S.C.I. 1909, **28**, 257. D.R.P. 223793, 1907, being Add. to D.R.P. 210519. Aust. P. 51094, 1908. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, (4), **60**, 173. U. S. P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, (4), **60**, 54. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538; Wagn. Jahr. 1904, II, 394, D.R.P. 159524, 1901; abst. Chem. Centr. 1905, **76**, [(5), **9**], II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; Wagn. Jahr, 1905, II, 190; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. Aust. P. 31391. It. P. 62042, 1901. E.P. 309, 1911; abst. J.S.C.I. 1911, **30**, 484. E.P. 29246, 1910; abst. J.S.C.I. 1911, 30, 888; C.A. 1911, **5**, 3340. F.P. 424621, 1911; abst. J.S.C.I. 1911, **30**, 741. F.P. 423774, 1910; abst. J.S.C.I. 1911, **30**, 615. U.S.P. 1046729; abst. Mon. Sci. 1913, **79**, 107; C.A. 1913, **7**, 700. D.R.P. 249535, 1910; abst. C.A. 1912, **6**, 3183. Hung. P. 3096, June 30, 1910. Swiss. P. 53777; abst. Kunst. 1912, **2**, 255. Belg. P. 231853, 1911. Aust. P. 54512, 1912; abst. Kunst. 1912, **2**, 393. Can. P. 134164, 1911.

4. E.P. 309, 1911; abst. J.S.C.I. 1911, **30**, 484. E.P. 29246, 1910; abst. J.S.C.I. 1911, **30**, 888; C.A. 1911, **5**, 3340. F.P. 424621, 1911; abst. J.S.C.I. 1911, **30**, 741. F.P. 423774, 1910; abst. J.S.C.I. 1911, **30**, 615. U.S.P. 1046729; abst. C.A. 1913, **7**, 700. D.R.P. 249535, 1910; abst. C. A. 1912, **6**, 3183. Hung. P. Appl. 3096, June 30, 1910. Swiss. P. 53777, abst. Kunst. 1912, **2**, 255. Belg. P. 231853, 1911. Aust. P. 54512, 1912; abst. Kunst. 1913, **3**, 393. U.S.P. 888516, 1908; abst. J.S.C.I. 1908, **27**, 683; C.A. 1908, **2**, 2866. U.S. P. 904269, 1908; abst. J.S.C.I. 1908, **27**, 1202. E.P. 4597, 1906; abst. J.S.C.I. 1907, **26**, 146. E.P. 592, 1907; abst. J.S.C.I. 1908, **27**, 73; C.A. 1908, **2**, 2018. D.R.P. 175664, 1903; abst. Zts. ang. Chem.

also an excellent precipitant. Other amyl esters which are solvents or plastic-inducing bodies are the lactate,[1] myristate, palmitate,[2] silicate and stearate. Those of higher molecular weight are feeble. Amyl silicate as well as methyl or ethyl silicates are acetate softeners in conjunction with other liquids, and are the most valuable of the solvent members of the so-called "silicic ethers,"[3] which have, for some years, been used to dissolve and decrease the inflammability of nitrocellulose.[4] The tendency to decomposition of the silicates is the serious drawback to their extended application.

Of the dihydric alcoholic esters, ethylene glycol diacetate is an excellent cellulose acetate solvent and gelatinizing liquid either cold or warm, and alone or in the presence of alcohol or acetone. Butyleneglycol acetate is equally efficient. Their disadvantage is a slight solubility in water, and a well marked hygroscopicity. The esters of the tri-hydric alcohol, glycerol, both mono-, di-, and tri-acetates, are excellent solvents and softeners, although they have the drawbacks of partial solubility in water, and are hygroscopic.[5] The formins, both mono-, di- and tri-formin, are of but little value as acetate softeners. Triacetin (glyceryl triacetate) as a solvent[6] and

1907, **20**, 461. D.R.P. 169782, 1904. D.R.P. 182773, 1904; abst. Zts. ang. Chem. 1907, **20**, 2090. E.P. 14483, 1903; abst. J.S.C.I. 1903, **22**, 1345.

1. U.S.P. 999490, 1911; abst. J.S.C.I. 1911, **30**, 1051.

2. U.S.P. 962877, 1910; abst. J.S.C.I. 1910, **29**, 940.

3. E.P. 14293, 1910; abst. J.S.C.I. 1911, **30**, 1171.

4. D. Bachrach, U.S.P. 794581, 1905; abst. J.S.C.I. 1905, **24**, 901.

5. Spirosal (glycol monosalicylate), a heavy, colorless, agreeably smelling liquid, dissolves partially hydrated acetylcellulose in the cold, more readily by warming. Combination of glycol with many organic acids results in the formation of acetylcellulose solvents, either alone or in conjunction with alcohol or acetone. Included under this heading are the glycol esters of anthranilic, toluic, salicylic, vanillic, mandelic, naphthoic, phthalic, gallic, oxalic, malonic, succinic, tartaric, malic, aspartic and aconitic acids. Mesotan (methyloxymethyl ester of salicylic acid), thyresol (methyl ether of santal oil), amyl nitrite, amyl nitrate, and menthol and acetylsalicylate (D.R.P. 244787, 1910; abst. J.S.C.I. 1912, **31**, 511), are feeble solvents, whose dissolving power is increased upon the addition of methyl or ethyl alcohol.

6. U.S.P. 1015155, 1912; abst. Mon. Sci. 1912, **77**, 163. Swiss P. 52437; abst. Kunst. 1912, **2**, 135. Aust. P. 47889.

as a softener[1] is superior to monoacetin or diacetin.[2] A plastic of cellulose acetate and acetin[3] either with or without nitrocellulose[4] may be formed by warming acetin and cellulose ester together, thinning with an evaporative solvent to the desired consistency and total solids, masticating and forming into the desired shape. H. Manissadjian manufactures moulds and matrices from cellulose acetate[5] by adding a softening agent in various proportions, consisting of 5-20% castor oil, about an equal proportion of a sulphophenic derivative of a halogen and 10-15 parts glyceryl acetate. H. Danzer[6]

1. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 4642-10, June 21, 1909. For preparation of monochlorhydrin mono- and di-acetates, diacetin, acetochlorhydrin and iodohydrin diacetate, see R. Wegscheider and F. Zmerzlikar, Monatsh. 1913, **34**, 1061; abst. C.A. 1913, **7**, 3484. See G. Noyer, "Camphor Substitutes with Acetylcellulose," Caout. et Guttap., 1913, **10**, 6999; abst. Kunst. 1913, **3**, 353.

2. F.P. 432264, 1911: abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

3. E.P. 19735, 1908; abst. J.S.C.I. 1910, **29**, 18. F.P. 393963, 1908; abst. J.S.C.I. 1909, **28**, 257. D.R.P. 223793, being Add. to D.R.P. 210519. Aust. P. 51094, 1908.

4. E.P. 19735, 1908; abst. J.S.C.I. 1910, **29**, 18. F.P. 393963, 1908; abst. J.S.C.I. 1909, **28**, 257. D.R.P. 223793, 1907, being Add. to D.R.P. 210519. Aust. P. 51094, 1908. F.P. 438649, 1912; abst. J.S.C.I. 1912, **31**, 584; Kunst, 1912, **2**, 439. D.R.P. 228867, 1907; abst. J.S.C.I. 1911, **30**, 21; Chem. Zts. 1910, **9**, 2138; Zts. ang. Chem. 1910, **23**, 2398; Chem. Ind. 1910, **33**, 797; Chem. Tech. Rep. 1910, **34**, 638. F.P. 417027, 1910; abst. J.S.C.I. 1910, **29**, 1373. D.R.P. 240188, 1909; abst. Zts. ang. Chem. 1911, **24**, 2336; Wagn. Jahr. 1911, II, 468; Chem. Zentr. 1911, II, 1563; C.A. 1912, **6**, 2178; Chem. Tech. Rep. 1911, **35**, 576. F.P. 397429, 1908; abst. J.S.C.I. 1909, **28**, 812.

5. F.P. 397429, 1908; abst. J.S.C.I. 1909, **28**, 812.

6. F.P. 443031, 1911. U.S.P. 1089910, 1914; Swiss. P. 63585, 1911; abst. J.S.C.I. 1912, **31**, 1008; 1914, **33**, 375; C.A. 1914, **8**, 1551, 2252. E.P. 13239, 1912; abst. Kunst. 1913, **3**, 73; C.A. 1913, **7**, 3840. Diphenylglyceryl ether may be obtained from the dichlorhydrins and sodium phenylate; phenylglycide from epichlorhydrin and sodium phenolate; chlorinated diphenylglyceryl ethers from the dichlorhydrins and chlorinated sodium phenolate; and dicresylglyceryl ethers from the dichlorhydrins and sodium cresolates. In this connection see L. Clement and C. Riviere, Kunst. 1912, **2**, 436. See also G. Noyer (Caout. et Guttap. 1913, **10**, 7297, 7362; L'Ind. Cinem.

prepares plastic cinematographic films by the use of acetin alone as a softener, or in combination with such bodies as diphenylglyceryl ethers, phenylglycid, dicresylglyceryl ether or their chlor-derivatives. For these compounds are claimed a low volatility, negligible hygroscopicity, good plasticity, and permanency in the light and air. The plastic mass of the Compagnie Francaise du Celluloid [1] comprises tri-acetylated glycerol, magnesium chloride and tricresyl-phosphate, thinned to the desired consistency with alcohol, acetone or tetrachlorethane. A. Eichengruen [2] combines dichlorhydrin and acetin to prepare mouldable cellulose acetate objects. For the uses of acetins with cellulose acetate see a lengthy paper by G. Noyer, in which properties and methods of manufacture of the simple and mixed formins and acetins are given.[3] Bergamot oil will gelatinize hydrated cellulose acetate in the cold, and M. Salamon and W. Seaber [4] have shown this oil to contain considerable quantities of glyceryl acetate. Artificial essential oil of jasmine flowers, comprising a mixture of benzyl acetate, linalyl acetate, linalool and benzyl alcohol, is an active solvent [5] but too costly. The nitroacetins, prepared by nitrating acetin, as by the process of V. Vender,[6] whereby

1913, **2**, 165; abst. C.A. 1913, **7**, 4968; 1914, **8**, 821), for the formins (glyceryl formates), oxalins (glyceryl oxalates), monoformin, diformin, epiformin, epidiformin, triformin, acetin-formins, acetin-monoformin, acetin diformin and the nitroformins as camphor substitutes. For the esterification of glycerol by acetic acid in the presence of catalytic agents, see J. Senderens and J. Aboulenc, Compt. rend. 1914, **158**, 581; abst. C.A. 1914, **8**, 1752.

1. F.P. 440955, 1911; abst. Kunst. 1912, **2**, 355; Mon. Sci. 1914, **80**, 14.

2. U.S.P. 1015155, 1912; abst. Mon. Sci. 1912, **77**, 163. Swiss P. 52437; abst. Kunst. 1912, **2**, 135. Aust. P. 47889.

3. Caoutchouc and Gutta-Percha, 1913, **10**, 6875, 6990, 7009; abst. C.A. 1913, **7**, 2681, 2682; Kunst. 1913, **3**, 15.

4. Perf. Essent. Oil Record, **3**, 275; abst. C.A. 1913, **7**, 863.

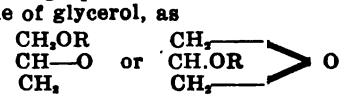
5. Heine & Co., D.R.P. 132425, 1899; Zts. ang. Chem. 1902, **15**, 720; Chem. Zentr. 1902, II, 474; Wagn. Jahr, 1902, 136; Chem. Zts. 1902-3, **2**, 221, 466, 898; J.S.C.I. 1902, **21**, 1096. See also J.S.C.I. 1901, **20**, 1137. Diethyl phthalate D.R.P. 227667, 1909; abst. Zts. ang. Chem. 1910, **23**, 2348; Chem. Zentr. 1910, II, 1579; Chem Tech. Rep. 1910, **34**, 596), is a solvent for resins, oils and acetated cellulose and is known in the trade as "Avolin."

6. D.R.P. 209943, 1906; abst. J.S.C.I. 1909, **28**, 675; abst. Chem. Zentr. 1909, **80**, 1839; Zts. ang. Chem. 1909, **22**, 1614; Wagn. Jahr. 1909, II, 540; Chem. Ind. 1909, **32**, 315.

pure nitroacetin is obtained in good yield by nitrating acetin by a nitro-sulfuric acid mixture containing more nitric than sulfuric acid. The nitroacetins and nitroformins are not as energetic acetate solvents, as before the nitro group is introduced. Mono- or poly-glyceryl esters of benzoic, salicylic, phthalic or phthalonic acids, especially glyceryl monobenzoate[1] dissolved in acetone are claimed as solvents by H. Dreyfus. More rigid products are obtained by using smaller proportions of the glyceryl benzoate. According to the Badische Anilin and Soda Fabrik[2] esters of cyclohexanol, of cyclopentanol or of their homologues or derivatives, are useful solvents of celluloid or cellulose esters for the preparation of varnishes.

Of the mono-hydroxy carbocyclic acetic esters, phenyl acetate (phenoxyacetic ether) proposed by F. Bayer & Co.[1] has shown the same disadvantages as when used as a nitrocellulose solvent, i. e., a tendency to decompose with the liberation of phenol, and to turn red when exposed to the light. Although aniline is an excellent solvent, the acetation to aniline acetate destroys its solvent power. Benzyl acetate is more stable than phenyl acetate, and a more energetic softening agent for acetylcellulose. Closely allied is benzyl benzoate, which has been patented by W. Lindsay as a solvent for nitrocellulose[3] and by H. Dreyfus[4] for acetylcellulose. Balsams

1. F.P. 461544, 1913; abst. J.S.C.I. 1914, **33**, 196. The Compagnie Gen. de Phon. Cinemato. et Apparells de Precision (Swiss. P. 61929, 1912; abst. C.A. 1914, **8**, 2124. U.S.P. 1089910, 1914; abst. Kunst. 1914, **4**, 275), prepare a flexible compound for the manufacture of cinematographic films from a solution of acetylcellulose in an ether oxide of glycerol, as



2. F.P. 440733, 1912; abst. J.S.C.I. 1912, **31**, 828.

3. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909.

4. U.S.P. 961360, 1910; abst. J.S.C.I. 1910, **29**, 875. F.P.

of Peru and tolu, which consist mainly of benzyl benzoate, benzyl cinnamate and cinnamyl benzoate, gelatinize cellulose acetate upon heating, more so in the presence of alcohol. Tolyl acetate, cresyl acetate and xylyl acetate exert but a weak solvent action. Of the di-hydric carbocylic alcoholic esters, resorcinol diacetate, a heavy, non-volatile, difficultly water-soluble oil, dissolves both normal and partial hydrated cellulose acetate with ease in the cold. L. Lederer[1] has found resorcinol diacetate especially valuable in the manufacture of continuous photographic films, the diacetate being added in the proportion of 1-2% calculated on the weight of the film, and preferably dissolved in ethyl acetate. Pyrogallol triacetate—the best known example of trihydric carbocyclic alcoholic ester of a monobasic fatty acid—may readily be prepared from pyrogallol, acetic acid, acetic anhydride and a trace of catalyzer as sulfuric acid, is an excellent solvent and softener, but has a marked tendency to decompose with the liberation of acetic acid upon standing. Acetated pyrogallol comes into commerce as the mono-acetate called Eugallol, and the tri-acetate known as Lenigallol. Pyrogallol di-salicylate (Saligallol), chrysarobin triacetate (Eurobin), chrysarobin tetra-acetate (Lenirobin) and resorcinol monoacetate (Euresol), are

416843, 1910; abst. J.S.C.I. 1910, **29**, 875. See Celluloid Co., D.R.P. 236056, 1910; C.A. 1913, 7, 3840. E.P. 13692, 1910; abst. J.S.C.I. 1911, **30**, 279. For preparation of benzyl salicylate, see E.P. 25735, 1899; of glyceryl salicylate, see C. Sorger, F.P. 373854, 1907; abst. J.S.C.I. 1907, **26**, 778; and of glyceryl monocinnamate, see D.R.P. 235357, 1910; abst. Zts. ang. Chem. 1911, **24**, 1435; Chem. Zentr. 1911, II, 171; Chem. Tech. Rep. 1911, **35**, 348; Wagn. Jahr. 1911, II, 97. U.S.P. 999955, 1000040, 1911; abst. J.S.C.I. 1911, **30**, 1088.

1. E.P. 8945, 1909; abst. J.S.C.I. 1909, **28**, 1271. F.P. 402083, 1909; abst. J.S.C.I. 1909, **28**, 1270; Mon. Sci. 1910, (4), **73**, 168. Upon proper manipulation, propyl, butyl and amyl benzoates and anthranilates will dissolve partially hydrated acetyl cellulose. D.R.P. Anm. L-30386, June 6, 1910. Resorcinol diacetate is a heavy, strongly refractive liquid which may readily be prepared by combining reacting weights of resorcinol with acetic anhydride, the alcohol having first been dissolved in the least amount of glacial acetic acid. Upon the addition of a small amount of condensing agent, as sulfuric acid, there is a rapid rise of temperature. After standing several hours, precipitate the ester by a large volume of cold water, wash to neutrality and dehydrate. It is an energetic simple solvent in the cold of acetone-soluble hydrated cellulose acetate. The yield is about 120% by weight of the resorcinol taken.

all solvents, but they apparently, as yet, have been but little investigated. The tetra-hydroxy alcohol, erythrol, the penta-hydric alcohol, arabite, and the hexa-hydric alcohol, mannitol, all form acetates, but they are readily soluble in water, and while they display a softening action on hydrated acetylcellulose, their action, combined with high cost, has never brought them into industrial use. Pyragallol triacetate may be changed into galloacetophenone diacetate [4] which dissolves the acetone-soluble ester.

H. Mork has described cellulose acetate compositions made with methyl chloracetate,[1] a colorless liquid boiling at 129°, and miscible in all proportions with ethyl acetate, chloroform, alcohol, acetone or acetylene tetrachloride. The acetylcellulose solutions are claimed to flow rapidly, film easily, and leave upon evaporation in thin layers, smooth transparent films. Ethylchloracetate has been patented by the Chemische Fabrik von Heyden [2] for the same purpose, the advantage of the ethyl over the methyl ester being slower evaporation, lower volatility and more uniform drying of the films. Both A. Wohl [3] and H. Mork [4] have discovered that methyl formate, a highly volatile liquid boiling at about 32°, which is the ester formed by the condensation of methyl alcohol and formic acid

1. U.S.P. 1039782, 1912; abst. J.S.C.I. 1912, **31**, 1027; C.A. 1912, **6**, 3917; Mon. Sci. 1913, **79**, 110. For rearrangement of pyrogallol triacetate, see G. Heller, Ber. 1913, **45**, 2389; abst. C.A. 1913, **7**, 83. For manufacture of pyrogallol triacetate, see L. Lederer, D.R.P. 124408, 1901; abst. Jahr. Chem, 1901, II, 1165; Wagn. Jahr. 1901, II, 10; Zts. ang. Chem. 1901, **14**, 1141; Chem. Zentr. 1901, II. 903; Chem. Zts. 1901-2, **1**, 112, 379. He mixes 200 parts of pyrogallol with 500 parts acetic anhydride, and 1 part of conc. sulfuric acid. Heat is evolved, while the precipitation of crystalline triacetate soon commences. The sulfuric acid may be replaced by gaseous HCl, or aqueous phosphoric acid.

2. D.R. Anm. C-22897, 1913; abst. Kunst. 1913, **3**, 279, 318.

3. E.P. 3139, 1911; abst. J.S.C.I. 1911, **30**, 888; Chem. Tech. Rep. 1911, **85**, 520. F.P. 425900, 1911; abst. J.S.C.I. 1911, **30**, 951. D.R.P. 246651, 1910; abst. C.A. 1912, **6**, 2529; Chem. Tech. Rep. 1912, **36**, 332; Zts. ang. Chem. 1912, **25**, 1549; Chem. Zentr. 1912, **83**, 1742. Belg. P. 232699, 1911. Aust. P. 29b, A-403, 1911, Mar. 12, 1910; Jan. 14, 1911. D.R.P. 246657, 1910; abst. Kunst. 1912, **2**, 232. Knoll & Co. (D.R.P. 276013, 1912) employ methyl-, ethyl-, propyl-, and *b*-naphthol-benzoates (benzonaphthol in conjunction with ethyl tartrate and oleic acid in the production of plastic effects.

4. U.S.P. 972464, 1910; abst. J.S.C.I. 1910, **29**, 1245; Mon. Sci. 1911, (5), **74**, 12; Chem. Tech. Rep. 1911, **85**, 152.

with the elimination of water, is also a very excellent solvent for cellulose acetate, and with it solutions of cellulose acetate can be made of a concentration comparable with those produced with chloroform; for example, cellulose acetate of a quality from which can be produced tough films can be easily dissolved in methyl formate in the proportion of at least 24 oz. of cellulose acetate to 1 gal. methyl formate. Methyl formate has distinct advantages over chloroform. It is not necessary for all purposes that methyl formate be used alone as a solvent for the cellulose acetate, for it may be desirable to modify the rate of evaporation of the solvent, which may be done by adding to the methyl formate a less volatile solvent such as acetylene tetrachloride or phenol. To solutions of cellulose acetate in methyl formate can be added limited quantities of liquids which are non-solvents of cellulose acetate; as, for example, benzol or carbon tetrachloride, such non-solvents modifying the rate of evaporation and also serving as diluents.

Glycol benzoate,[1] glycol cinnamate,[2] glyceryl cinnamate,[3] *m*-cresyl butyrate and *m*-cresyl isovalerate,[4] when prepared according to the patentees directions either alone or with ethyl alcohol, has not given in the author's hands solvents of commercial value. L. Behrend[5] has described plastics composed of aniline resinate and acetated cellulose. The addition of benzylidineacetoacetic ester either with or without the addition of ethylbenzyl-*o*-toluidine or acetylbenzyl-*o*-toluidine to noninfllammable cellulose esters, result in the formation of plastics peculiarly useful for the formation of lustrous threads and bands.[6] In addition to the cresols for combination with

1. U.S.P. 1014859, 1912.
2. U.S.P. 1000040, 1911.
3. U.S.P. 999955, 1911.
4. U.S.P. 1033841, 1912.
5. U.S.P. 952724, 1910; abst. J.S.C.I. 1910, **29**, 503. E.P. 4154, 1909; abst. J.S.C.I. 1910, **29**, 100. F.P. 402028, 1909; abst. J.S.C.I. 1909, **28**, 1212. D.R.P. 242467, 1908; abst. Kunst. 1912; **2**, 59; C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **86**, 111.
6. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909.

acetylcellulose as softening bodies [1] or for artificial silk formation,[2] the cresol acetates have been described as valuable in conjunction with a volatile solvent for imparting temporary plasticity.[3] Ethylchlorstearate,[4] ethyl myristate and ethyl palmitate have been advocated, but the high molecular weight of the acid radicals decreases the power of solution, and they are of little practical value. Ethyl phthalate has been claimed by L. Lilienfeld [5] as an excellent agent for combining with cellulose acetate in the production of impressions on textile fabrics which are fast to water and possess the required suppleness and flexibility. Either nitrocellulose or acetylcellulose is dissolved in acetone together with an equal weight or more of ethyl phthalate. Of the lactic esters, ethyl lactate [6]

1. U.S.P. 695127, 1902. Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303. U.S.P. 792149, 1905; abst. J.S.C.I. 1905, **24**, 799; Mon. Sci. 1906, (4), **64**, 22. F.P. 385179, 385180, 1907; abst. J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 105, 106; Bull. Soc. Chim. 1909, (4), **6**, 557. F.P. 432047, 1911; abst. J.S.C.I. 1912, **31**, 24. First Add. 15719, to F.P. 432047; abst. J.S.C.I. 1912, **31**, 1027; Kunst. 1912, **2**, 415. Belg. P. 241252, 1911. E.P. 20976, 1911.

2. E.P. 8646, 8647, 1910; abst. J.S.C.I. 1911, **30**, 533, 616, Chem. Tech. Rep. 1911, **35**, 307. F.P. 413657, 413658, 1910; abst. J.S.C.I. 1910, **29**, 1101. F.P. 414679, 414680, 1910; abst. J.S.C.I. 1910, **29**, 1199, 1228. Swiss. P. 51644, 51910; abst. Kunst. 1912, **2**, 77, 99. Belg. P. 223996, 1910. Aust. 47244. Aust. 53109; abst. Kunst. 1912, **2**, 255.

3. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

4. U.S.P. 962877, 1910; abst. J.S.C.I. 1910, **29**, 940.

5. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909. U.S.P. 888516, 1908; abst. J.S.C.I. 1908, **27**, 683; C.A. 1908, **2**, 2866. U.S.P. 904269, 1908; abst. J.S.C.I. 1908, **27**, 1202. E.P. 4597, 1906; abst. J.S.C.I. 1907, **26**, 146. E.P. 592, 1907; abst. J.S.C.I. 1908, **27**, 73; C.A. 1908, **2**, 2018. E.P. 14483, 1903; abst. J.S.C.I. 1903, **22**, 1345. D.R.P. 175664, 1903; abst. Zts. ang. Chem. 1907, **20**, 461. D.R.P. 169782, 1904. 182773, 1904; abst. Zts. ang. Chem. 1907, **20**, 2090.

6. U.S.P. 1015156, 1912; abst. Mon. Sci. 1912, **77**, 163. E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1005; Chem. Tech. Rep. 1911, **35**, 340. E.P. 18076, 1910, being First Add. to E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1199. F.P. 412797, 1910; Rev. Chim. Ind. 1910, **21**, 257; abst. J.S.C.I. 1910, **29**, 1005. First Add. 12388, Mar. 19,

of amyl lactate[1] are suitable. Lactic acid alone is an excellent solvent for cellulose acetate,[2] and numerous combinations,[3] especially among the earlier formulas are found in which the entire plasticity was due to lactic acid. The disadvantages of lactic acid are a decided hygroscopicity, and acid reaction. Methyl myristate,[4] methyl oxalate,[5] dimethyl oxalate, methyl palmitate, methyl phthalate,[6] methyl silicate, methyl stearate and methyl *p*-toluenesulfonate have little if any advantages over the corresponding ethyl esters previously mentioned. The naphthyl acetates are valuable softeners in conjunction with high-boiling solvents as acetylene tetrachloride, coupled with gentle heat.[7] Phenol sulfonate,[8] and mixed phenol esters,[9] have been described. Sulforicinic acid,

1910. D.R.P. 238348, 1909; abst. C.A. 1912, **6**, 1672; Chem. Zentr. 1911, **82**, 1085; Chem. Ind. 1911, **34**, 637; Chem. Tech. Rep. 1911, **35**, 520. Aust. P. 47899. Swiss. P. 52115; abst. Kunst. 1912, **2**, 99. Can. P. 129265, 1910.

1. U.S.P. 999490, 1911; abst. J.S.C.I. 1911, **30**, 1051.

2. F.P. 421854, 1909; abst. J.S.C.I. 1911, **30**, 416.

3. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264, 1911; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911. U.S.P. 1029341, 1912; abst. J.S.C.I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164. E.P. 8313, 1911; abst. J.S.C.I. 1911, **30**, 1050; Chem. Tech. Rep. 1911, **35**, 556; 1912, **36**, 532; C.A. 1912, **6**, 3018. F.P. 428069, 1911; abst. J.S.C.I. 1911, **30**, 1156. Aust. Appl. 2994, 1911. U.S.P. 690211, 1901; abst. J.S.C.I. 1902, **21**, 272.

4. U.S.P. 962877, 1910; abst. J.S.C.I. 1910, **29**, 940.

U.S.P. 738533, 1903; abst. J.S.C.I. 1903, **22**, 1100. E.P. 26075, 1901; abst. J.S.C.I. 1902, **21**, 1469. F.P. 317008, 1901; abst. J.S.C.I. 1902, **21**, 873.

5. U.S.P. 962877, 1910; abst. J.S.C.I. 1910, **29**, 940.

6. U.S.P. 738533, 1903; abst. J.S.C.I. 1903, **22**, 1100. E.P. 26075, 1901; abst. J.S.C.I. 1902, **21**, 1469. F.P. 317008, 1901; abst. J.S.C.I. 1902, **21**, 873.

7. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909. U.S.P. 729990, 1903; abst. J.S.C.I. 1903, **22**, 817. D.R.P. 162239, 1902; abst. Zts. ang. Chem. 1906, **19**, 498; Chem. Centr. 1905, II, 1000.

8. E.P. 8646, 8647, 1910; abst. J.S.C.I. 1911, **30**, 533, 616; Chem. Tech. Rep. 1911, **35**, 307. F.P. 413657, 413658, 1910; abst. J.S.C.I. 1910, **29**, 1101. F.P. 414679, 414680, 1910; abst. J.S.C.I. 1010, **29**, 1199, 1228. Swiss P. 51644, 51910; abst. Kunst. 1912, **2**, 77, 99. Belg. P. 223996, 1910. Aust. P. 47244. Aust. P. 53109; abst. Kunst. 1912, **2**, 255.

acetated castor oil,[1] toluenesulfonic esters,[2] amyl valerianate, ethyl oenanthate, propyl benzoate and butyl benzoate have a slow dissolving action, especially in the presence of alcohol and heat. The following are non-solvents of both chloroform-soluble and acetone-soluble acetylcellulose: Amyl butyrate, ethyl benzoate, ethyl butyrate, ethyl valerianate, amyl valerianate, ethyl sebacate and acetated turpentine.

Nitro and Amido Solvents. Acetamide[3] has, like urea,[4] guanidine, methylamine[5] and diethyldiphenyl urea[6] been

9. F.P. 385179, 385180, 1907; abst. J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 105, 106; Bull. Soc. Chim. 1909, (4), **6**, 557. F.P. 432047, 1911; abst. J.S.C.I. 1912, **31**, 24. First Add. 15719, to F.P. 432047; abst. J.S.C.I. 1912, **31**, 1027; Kunst. 1912, **2**, 415. Belg. P. 241252, 1911. E.P. 20976, 1911.

1. U.S.P. 712200, 1902; abst Mon. Sci. 1903, (4), **60**, 165.

2. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264, 1911; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

3. L. Lederer, U.S.P. 774677, 1904; abst. J.S.C.I. 1904, **23**, 1159. E.P. 7088, 1902; abst. J.S.C.I. 1903, **22**, 563. F.P. 319724, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Add. 811, dated Mar. 18, 1902, to F.P. 319724; abst. J.S.C.I. 1903, **22**, 563. D.R.P. 145106, 1902; abst. Jahr. Chem. 1904, 1168; Mon. Sci. 1904, (4), **60**, 93; Zts. ang. Chem. 1903, **16**, 1090; Chem. Centr. 1903, II, 1155. D.R.P. 151918, 1902, Add. to D.R.P. 145106; abst. Chem. Centr. 1904, II, 1180; Jahr. Chem. 1904, 1168. D.R.P. 152111, 1902; abst. Zts. ang. Chem. 1904, **17**, 1250; Chem. Zentr. 1904, II, 382; Wagn. Jahr. 1904, II, 512; Jahr. Chem. 1904, 1168. See D.R.P. 189703, being Add. to D.R.P. 152111; abst. Chem. Zentr. 1907, II, 1822; Chem. Tech. Rep. 1907, **31**, 570; Wagn. Jahr. 1907, II, 562; Chem. Zts. 1907, **6**, No. 387; Mon. Sci. 1910, (4), **73**, 159.

4. W. Lindsay, U.S.P. 1045990, 1913; abst. Mon. Sci. 1913, **79**, 110; J.S.C.I. 1913, **32**, 19; C.A. 1913, **7**, 699. U.S.P. 1050065, 1913; abst. Mon. Sci. 1913, **79**, 107; J.S.C.I. 1913, **32**, 133; Kunst. 1913, **3**, 218. U.S.P. 1067785, 1913; abst. Kunst. 1913, **3**, 455; Mon. Sci. 1914, **80**, 38; J.S.C.I. 1913, **32**, 823; C.A. 1913, **7**, 3025. E.P. 10794, 10795, 1910; abst. J.S.C.I. 1911, **30**, 205, 679. F.P. 415517, 415518, 1910; abst. J.S.C.I. 1910, **29**, 1299; Mon. Sci. 1912, **77**, 9. U.S.P. 1027619, 1912; abst. J.S.C.I. 1912, **31**, 583; Mon. Sci. 1912, **77**, 163. The acetylation of urea to an acetate does not increase the solvent power for hydrated cellulose acetate, nor is urea acetate an auxiliary solvent in conjunction with acetone or tetrachlorethane. Some of the substituted ureas, however, are energetic solvents, specifically diethylmalonyl urea (veronal, diethylbarbituric acid), a white, crystalline powder, m. pt. 191°, and soluble in about 150 parts cold and 12 parts boiling water. Veronal is readily soluble in acetone, and such solutions make useful additions to acetate plastics.

5. E.P. 26502, 1906; abst. J.S.C.I. 1907, **26**, 634. F.P. 371357, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 79. Belg. P. 195839, 1906.

6. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P.

used in cellulose acetate solutions as an ant-acid and preservative more than for their direct dissolving power. Diethylamine [1] is similar. Diethyldiphenyl urea and tetraphenyl urea [2] have been described as ant-acids in the nitrocellulose industry. Aniline and its homologues toluidine and xylidine, all liquids, are excellent solvents of partially hydrated cellulose acetate, the speed of solution diminishing with increasing molecular weight. As a direct solvent,[3] softener,[4] or plastic, either alone [5] or in combination with shellac,[6] it is used in cold or

18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909.

1. U.S.P. 891218, 1908; abst. J.S.C.I. 1908, **27**, 765; Mon. Sci. 1909, (4), **70**, 116. E.P. 2026-B, 1907; abst. J.S.C.I. 1908, **27**, 353, F.P. 373994, 1907; abst. J.S.C.I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 83; Chem. Tech. Rep. 1907, **31**, 302. D.R.P. 201233, 1906; abst. Chem. Zts. 1908, **7**, 993; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, 994; Jahr. Chem. 1905-08, II, 982; Chem. Ind. 1908, **31**, 587. D.R.P. 203178, 1906; abst. Chem. Zts. 1909, **8**, 1053; Zts. ang. Chem. 1908, **21**, 2426; Chem. Zentr. 1908, **79**, 1837; Jahr. Chem. 1905-08, II, 984; Chem. Ind. 1908, **31**, 741.

2. C. Claessen, D.R.P. 178133, 1906. E.P. 20037, 1906. F.P. 363090, 1906. Trimethyl-ethylene and diphenylmethane are non-solvents.

3. U.S.P. 1005454, 1911; abst. J.S.C.I. 1911, **30**, 1249. E.P. 476, 1910; abst. J.S.C.I. 1910, **29**, 1082. F.P. 411298, 1910; abst. J.S.C.I. 1910, **29**, 978; Phot. Ind. 1910, 1221; Eders Jahr. 1911, 526. Aust. P. 50656, 1910; abst. Kunst. 1912, **2**, 77. Phot. Ind. 1911, 28; Eders Jahr. 1911, 526. Belg. P. 222106, 1910. Hung. Anm. M-3691, Dec. 30, 1909. Swiss P. 51839, 1910; abst. Kunst. 1912, **2**, 77.

4. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909.

5. U.S.P. 774677, 1904; abst. J.S.C.I. 1904, **23**, 1159. E.P. 7088, 1902; abst. J.S.C.I. 1903, **22**, 563. F.P. 319724, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Add. 811, dated Mar. 17, 1902, to F.P. 319724; abst. J.S.C.I. 1903, **22**, 563. D.R.P. 145106, 1902; abst. Jahr. Chem. 1904, 1168; Mon. Sci. 1904, (4), **60**, 93; Zts. ang. Chem. 1903, **16**, 1090; Chem. Centr. 1903, II, 1155. D.R.P. 151918, 1902. Add. to D.R.P. 145106; abst. Jahr. Chem. 1904, 1168; Chem. Centr. 1904, II, 1180. D.R.P. 152111, 1902.

6. U.S.P. 952724, 1910; abst. J.S.C.I. 1910, **29**, 503. E.P.

only moderately warm solutions to exert the maximum effect, and in combination with other more volatile solvents as acetone, ethyl acetate, chloroform or acetylene tetrachloride. The high boiling point (184°), 3% solubility in water, and proneness to discoloration upon standing, are the chief drawbacks to the use of aniline (phenylamine, amido-benzene). Of the phenyl-alkylamines, monomethyl-, dimethyl-, monoethyl- and diethyl-aniline are less energetic solvents, alkylation of the amine seemingly decreasing the solvent capacity with increase in molecular weight. The polyphenylamines, diphenylamine and triphenylamine, are both solids, and in alcoholic solution upon the application of heat, partially gelatinize the acetone-soluble acetate. Methylbenzyltrichloraniline and methylbenzoyltrichloraniline,[1] trichloraniline[2] and the nitranilines,[3] 4154, 1909; abst. J.S.C.I. 1910, **29**, 100. F.P. 402028, 1909; abst. J.S.C.I. 1909, 28, 1212. D.R.P. 242467, 1908; abst. Kunst. 1912, **2**, 59. C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 111.

1. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909.

2. U.S.P. 1015156, 1912; abst. Mon. Sci. 1912, **77**, 163. E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1005; Chem. Tech. Rep. 1911, **35**, 340. E.P. 18076, 1910. First Add. to E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1199. F.P. 412797, 1910; abst. J.S.C.I. 1910, **29**, 1005; Rev. Chim. Ind. 1910, **21**, 257. First Add. 12388, dated Mar. 19, 1910, to F.P. 412797; abst. J.S.C.I. 1910, **29**, 1199. D.R.P. 238348, 1909; abst. Chem. Ind. 1911, **34**, 637; Chem. Tech. Rep. 1911, **35**, 520; Wagn. Jahr. 1911, II, 552; C.A. 1912, **6**, 1672; Chem. Zentr. 1911, **82**, 1085. Aust. P. 47899. Swiss P. 52115; abst. Kunst. 1912, **2**, 99. Can. P. 129265, 1910.

3. U.S.P. 961241, 1910; abst. J.S C.I. 1910, **29**, 876; Mon. Sci. 1910, (4), **73**, 135. U.S.P. 979966, 1910; abst. J.S.C.I. 1911, **30**, 206; Mon. Sci. 1912, **77**, 30. U.S.P. 981574, 1002408, 1911; abst. J.S.C.I. 1911, **30**, 126, 1157; Mon. Sci. 1912, **77**, 29. E.P. 24284, 1907; abst. J.S.C.I. 1908, **27**, 1150; Mon. Sci. 1911, (5), **74**, 92. F.P. 383636, 1907; abst. J.S.C.I. 1908, **27**, 332. First Add. dated April 5, 1909, to F.P. 383636; abst. J.S.C.I. 1909, **28**, 1199. E.P. 7743, 1909; abst. J.S.C.I. 1910, **29**, 209. D.R.P. 198008, 1907; abst. Chem. Zts. 1908, **7**, 865; Wagn. Jahr. 1908, II, 409; Zts. ang. Chem. 1908, **21**, 1471; Chem. Zentr. 1908, I, 1809; Chem. Tech. Rep. 1908, **32**, 379; Bull. Soc. Chim. 1909, (4), **6**, 557. D.R.P. 199559, 1907; abst. Zts. ang. Chem. 1908, **21**, 1810; Chem. Zentr. 1908, **79**, 271; Bull. Soc. Chim. 1909, (4), **6**, 557. D.R.P. 234028, 1908; abst. Zts. ang. Chem. 1911, **24**, 1151; Wagn. Jahr. 1911, II, 422.

are substituted anilids which have been proposed specifically as acetylcellulose softeners, most of them having been previously patented as pyroxylin plastic-inducing bodies. The Compagnie Francaise du Celluloid has protected by patent issuance a series of twenty compounds, which may be regarded as acetylethylaniline, in which the acetyl may be substituted by propionyl, butyl or valeryl radicals, and the ethylaniline [1] may be replaced by methyl-, propyl-, butyl- and amyl-anilines. In this series will be found excellent acetylcellulose gelatinizers, the solvent action being made more effective by dilution with acetone, tetrachlorethane or both. Anhydroformaldehyde aniline [2] has been especially employed in phenol-aldehyde condensation products with cellulose acetate. The anilids, of which acetanilid, first patented for nitrocellulose use, and subsequently as an acetate plastic, is perhaps the best known, are valuable in combination with acetone-soluble acetylcellulose, but reaches greater efficiency as a softening agent in some of its derivatives. W. Walker [3] combines directly with cellulose acetate preferably in presence of phenol, thymol or similar body. Cathelineau and Fleury [4] use acetanilid dissolved in

1. F.P. 427804, 1910; abst. J.S.C.I. 1911, **30**, 1051; C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 111.

2. U.S.P. 952724, 1910; abst. J.S.C.I. 1910, **29**, 503 E.P. 4154, 1909; abst. J.S.C.I. 1910, **29**, 100. F.P. 402028, 1909; abst. J.S.C.I. 1909, **28**, 1212. D.R.P. 242467, 1908; abst. Kunst. 1912, **2**, 59. C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 111.

3. U.S.P. 774713, 1904; abst. Mon. Sci. 1905, (4), **62**, 50; J.S.C.I. 1904, **23**, 1159; U.S.P. 774714, 1904; abst. J.S.C.I. 1904, **23**, 1159. Ethylaniline, ethyltoluidine and ethylxylidine with alcohol are excellent solvents of partially hydrated acetylcellulose, while phenyl isocyanide and phenyl sulfocyanate are solvents without the addition of alcohol.

4. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909. F.P. 354942, 1905; abst. J.S.C.I. 1905, **24**, 1169, Add. dated June 8, 1905, to F.P. 354942; abst. J.S.C.I. 1905, **24**, 1226. E.P. 12277, 12278, 1905; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185240, 1906; abst. Zts. ang. Chem. 1907, **20**, 2177; Chem. Zentr. 1907, **78**, 1037. D.R.P. 185241, 1906, Add. to D.R.P. 185240; abst. Chem. Zentr. 1907, **78**, 1819.

a low boiling solvent such as acetone. Tetrachlorethylacetanilid, trichlormethylacetanilid—usually in combination with triphenyl phosphate or tricresyl phosphate and dissolved in methyl alcohol [1] or ethyl alcohol [2] with the application of heat—have been described by W. Lindsay as efficient plastic compounds for acetylcellulose combination. The use of acetylmethylaniline (commercially known as "manol") by both H. Dreyfus [3] and A. Eichengruen [4] has been protected by patent grants. In the inflammable cellulose esters industry other similar amido compounds have been advocated, such as acetyldiphenylamine, acetyltolylxylylamine, amylidenedimethylether and amylidinediethylether,[5] formyldiphenylamine, acetylphenyltolylamine, and acetylphenylnaphthylamine,[6] amidines from *o*-diamines and not containing halogen, as methenyl-*o*-toluylenediamine,[7] and methylethenyltrichloramidine,[8] and methenyl-*o*-toluylenediamine (methenyl-3.4-toluylenediamine).[9] Ethyl-*o*-toluidine [10] in solvent action, is greater than toluidine, and about the equal of aniline. By acetylating alkylated toluidines, speed of gelatinization and solution is increased, methylacetyl-*o*-toluidine being especially

1. U.S.P. 1041117, 1912; abst. J.S.C.I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; C.A. 1912, **6**, 3518.

2. U.S.P. 1041118, 1912; abst. J.S.C.I. 1912, **31**, 1075. See D.R. Anm. L.-30181, 1910, L.-30386, 1910.

3. F.P. 432047, 1911; abst. J.S.C.I. 1912, **31**, 24. First Add. 15719, to F.P. 432047; abst. J.S.C.I. 1912, **31**, 1027; Kunst. 1912, **2**, 415. Belg. P. 241252, 1911. E.P. 20976, 1911; abst. C.A. 1913, **7**, 890; J.S.C.I. 1913, **32**, 80; Kunst. 1913, **3**, 175.

4. E.P. 27258, 1910; abst. J.S.C.I. 1911, **30**, 1112; C.A. 1912, **6**, 1526. Can. P. 129983, 1910.

5. Deutsche Zelluloid Fabrik, D.R.P. 132371, 1903; F.P. 312817, 1901.

6. E.P. 12863, 1901. o-Nitrotoluol is a solvent for partially hydrated cellulose acetate in conjunction with alcohol. Chloracetone is a direct solvent in the cold.

7. E.P. 10228-A, 1906.

8. F.P. 366106, 1906.

9. E.P. 8077, 1906; abst. J.S.C.I. 1906, **25**, 608.

10. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909.

useful. *b*-Naphthylamine, *a*-naphthylaminedihydrocarvone,[1] and nitronaphthalin,[2] are the principal naphthalene derivatives which have been proposed as acetylcellulose solvents and softeners. Pyridine and its homologues quinoline and acridine, the latter a solid, has been used not only as a neutralizant in acetation,[3] but as a constituent of acetate lacquers,[4] preferably in conjunction with tetrachlorethane.[5] The use of pyridine acid sulfate in the acetation of cotton is on account of the sulfuric acid split off. F. Bayer & Co. have described the preparation of pyridine-soluble cellulose acetates.[6] Benzidin and dianisidin,[7] nitrochlorbenzene, nitrotoluene,[8] phthalimide[9]

1. D.R.P. 202720, 1907; abst. J.S.C.I. 1908, **27**, 1220; Zts. ang. Chem. 1908, **21**, 2428; Chem. Zentr. 1908, **79**, II, 1837; Jahr. Chem. 1905-08, II, 993; Mon. Sci. 1912, **77**, 57; Wagn. Jahr. 1908, II, 540; Chem. Tech. Rep. 1908, **32**, 594.

2. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

3. F.P. 418347, 1909; abst. J.S.C.I. 1911, **30**, 96. Add. 15217, to F.P. 418347; abst. J.S.C.I. 1912, **31**, 651; Kunst. 1912, **2**, 316.

4. E.P. 6798, 1912; abst. J.S.C.I. 1912, **31**, 1016. F.P. 429788, 1911; abst. J.S.C.I. 1911, **30**, 1267; C.A. 1912, **6**, 2186; Oil, Paint and Drug Review, April 24, 1912; Chem. Tech. Rep. 1912, **36**, 63.

5. E.P. 20527, 1912. D.R.P. 139669, 1903; abst. Jahr. Chem. 1903, 1014; Chem. Ind. 1903, **26**, 167; Wagn. Jahr. 1903, **49**, II, 418. Zts. ang. Chem. 1903, **16**, 285; Chem. Centr. 1903, I, 744. D.R.P. 243581, 1908; abst. J.S.C.I. 1912, **31**, 381; C.A. 1912, **6**, 2316; Chem. Tech. Rep. 1912, **36**, 196; Zts. ang. Chem. 1912, **25**, 654; Chem. Ind. 1912, **35**, 190; Chem. Zentr. 1912, **83**, 695.

6. F.P. 418347, 1909; abst. J.S.C.I. 1911, **30**, 96. Add. 15217, to F.P. 418347; abst. J.S.C.I. 1912, **31**, 651; Kunst. 1912, **2**, 316.

7. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, **60**, (4), 17, 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, (4), **60**, 27, 54. Aust. P. 31391. It. P. 62042, 1901.

8. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst, 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

9. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b,

and *p*-toluene sulfamid,[1] although patented as acetate solvents and plastic-inducing bodies, have not been found satisfactory in the author's hands. E. Fisher[2] has described nitromethane, with a boiling point of 101°, as an excellent mixed solvent for both nitro- and acetyl-cellulose, either alone or in conjunction with other solvents and diluents. Pyridine, quinoline, picoline, lutidine, nicotine and collidine are all weak solvents in the cold of acetone-soluble acetylcellulose.

W. Lindsay has found[3] that nearly all of the so-called camphor substitutes possess the property of dissolving acetylcellulose when used in conjunction with ethyl alcohol, and may, with propriety, be grouped in the following three classes:

(1). Those substances which are non-solvents when melted or dissolved in either methyl or ethyl alcohol in the cold or at room temperature, such as triphenylphosphate, tricresylphosphate and naphthalene.

(2). Those substances which become solvents when melted but are non-solvents when dissolved in ethyl alcohol at room temperature, such as camphor, tetrachlorethyl acetanilid, trichlormethyl acetanilid, and trichlorpropyl acetanilid.

(3). Those which become solvents when melted, and are

4642-10, June 21, 1909.

1. U.S.P. 738533, 1903; abst. J.S.C.I. 1903, **22**, 1100. E.P. 26075, 1901; abst. J.S.C.I. 1902, **21**, 1469. F.P. 317008, 1901; abst. J.S.C.I. 1902, **21**, 873.

2. D.R.P. 201907, 1907; abst. J.S.C.I. 1908, **27**, 1174; C.A. 1909, **3**, 491; Chem. Zts. 1909, **8**, 1040; Zts. ang. Chem. 1908, **21**, 2427; Chem. Zentr. 1908, **79**, 1398; Bull. Soc. Chim. 1909, (4), **6**, 557; Jahr. Chem. 1905-08, II, 987; Wagn. Jahr. 1908, II, 364. For preparation of tetranitromethane, see A. Pictet and P. Genequand, Arch. Sci. Phys. Nat. 1903, (3), **15**, 234; abst. J.C.S. 1903, **84**, 305; Ber. 1903, **36**, 2225; J.C.S. 1903, **84**, 596. C. Claessen, D.R.P. 184229, 1905; abst. Zts. ang. Chem. 1907, **20**, 1194; Chem. Zentr. 1907, II, 366; Chem. Tech. Rep. 1907, **31**, 267; Wagn. Jahr. 1907, II, 34; J.S.C.I. 1908, **27**, 183; Jahr. Chem. 1905-08, II, 160. E. Berger, Compt. rend. **191**, 813; Bull. Soc. Chim. 1910, **9**, 26; abst. J.S.C.I. 1910, **29**, 899; F. Bayer and Co., E.P. 24299, 1909; F.P. 384079, 1907; abst. C.A. 1909, **3**, 1690. R. Schenck, D.R.P. 211198, 211199, 1908; abst. J.S.C.I. 1909, **28**, 815; C.A. 1909, **3**, 2205; Wagn. Jahr. 1908, II, 13, 14; Zts. ang. Chem. 1909, **22**, 1561, 1562; Chem. Zentr. 1909, II, 81, 488; Chem. Tech. Rep. 1909, **33**, 362. W. Steinkopf and G. Kirchhoff, Ber. 1909, **42**, 3438; abst. J.S.C.I. 1910, **29**, 1104; J.C.S. 1909, **96**, i, 754; Chem. Zentr. 1909, II, 1538; Jahr. Chem. 1910, 91; Bull. Soc. Chim. 1911, (4), **8**, 977.

3. U.S.P. 1041113, 1912.

also solvents when dissolved in methyl or ethyl alcohol in equal parts at room temperature, such as toluol-sulphonamid, ethyl-*p*-toluolsulphonamid, benzene-sulphonamid, ethyl acetanilid and methyl acetanilid. He claims a mixture composed of one part each by weight of ethyl alcohol and ethyl-*p*-toluolsulphonamid is a more powerful solvent for acetone-soluble acetylcellulose than a mixture of two parts by weight of ethyl alcohol and one part by weight of ethyl *p*-toluolsulphonamid, a rapidly decreasing solvent action being shown if the alcohol is increased beyond this proportion. To produce flowable solutions in the cold the above camphor substitutes are diluted with methyl or ethyl alcohol, with one or more of the following: Chloroform, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, acetochlorhydrin, ethyl chloracetate, ethyl acetate and di-acetochlorhydrin.

Essential Oils.. Most essential oils contain one or more members of the camphoroid class, oleoptens or steaoptens or esters, to which their solvent action for nitrocellulose has been attributed. Those partially hydrated cellulose acetates completely soluble in pure acetone do not dissolve in the volatile oils of amber, bergamot, camphor (light or heavy), celery, lemon, origanum, rosemary or sandal wood. Difficulty soluble in oils of cade, caraway seed and clove. Readily soluble in oils of cedar and pennyroyal. Those odoriferous bodies containing benzyl benzoate are solvents in the ratio of benzyl ester contained therein. Terpinol, turpentine, terebene, terpineol are all devoid of dissolving power. Terpin hydrate is a partial solvent for cellulose acetate when heated. Thymene and anisic aldehyde soften the partially hydrated ester, and their solvent action is increased by addition of alcohol, acetone or heat. The following in conjunction with alcohol completely dissolve, acetone-soluble acetylated cellulose—cinnamic aldehyde, cumene, methyl salicylate, safrol and styrone.

Other Cellulose Ester Plastic-Inducing Bodies. A large number of cellulose acetate solvents and softeners were first patented for use in connection with the earlier nitrocellulose art. Many of the thermo-plastic compounds which the following described bodies produce with the cellulose nitrates, have

upon investigation been found valuable in the uninflammable cellulose ester art, and hence the obvious value of their enumeration herewith. None of these substitutes have been able, as yet, to entirely replace camphor, which possesses properties desirable for celluloid manufacture unapproached in a like degree by any known chemical or combination. Camphor possesses the advantages of excellent gelatinizing power; energetic solvency for a wide range of cellulose nitrates; ready solubility in ethyl alcohol; high melting and boiling point; a characteristic odor not unpleasant and a low volatility in combination; a low power of crystallization and unaffected by light. Certain acidyl derivatives of aromatic or aliphatic secondary amines, such as chloracetanilid and the acetyl-, formyl-, and benzoyl-naphthylamines or methyl aniline do not readily gelatinize the cellulose esters. Treatment with solvents removes impurities which tend to color the plastic upon exposure to light.[1] Acetyldiphenylamine, formyldiphenylamine, acetylphenyltolylamine,[2] and acetyldiphenylamine with triphenyl phosphate, amylidenedimethyl ether and amylidenediethyl ether[3] are practically odorless and stable, but much less soluble in alcohol than camphor. By chlorinating or brominating *o*-diamines in such manner that two halogen atoms are introduced in the *o*-position relative to the nitrogen

1. Chem. Fab. Weiler-ter-Meer, E.P. 2817, 1905. E.P. 15435, 1904; abst. J.S.C.I. 1905, **24**, 686. E.P. 16271, 1906; abst. J.S.C.I. 1907, **26**, 989. F.P. 341556, 1904; abst. J.S.C.I. 1904, **23**, 880. F.P. 377671, 1906; abst. Mon. Sci. 1908, (4), **68**, 145; C.A. 1907, **1**, 2831: J.S.C.I. 1907, **26**, 1064. Can. P. 103036, 1907. Belg. P. 194836, 1906. See also E.P. 12863, 22662, 1901; 2817, 1906 Acetylphenyltolylamine is recommended. For complete resume of nitrocellulose plastic-inducing bodies, consult Part Two.

2. Deutsche Zelluloid Fabrik, E.P. 12863, 1901; abst. J.S.C.I. 1902, **21**, 494. D.R.P. 132371, 1903; Zts. ang. Chem. 1902, **15**, 720; Wagn. Jahr. 1902, 594. Only when the primary aromatic amines are used, is the plastic said to become opaque after a time. But the primary may be used in mixtures with the secondary amines. See also D.R.P. 80776; abst. Zts. ang. Chem. 1895, **8**, 397.

3. E. Franquet, F.P. 312817, 1901; abst. J.S.C.I. 1902, **21**, 134; Mon. Sci. 1903, (4), **59**, 12. For the nitrocellulose-casein plastics of E. Franquet, see D.R.P. 138783, 1901, and addition D.R.P. 139905, 1902, thereto; abst. Mon. Sci. 1904, (4), **60**, 92; Zts. ang. Chem. 1903, **16**, 166, 286; Chem. Centr. 1903, I, 485, 800; Jahr. Chem. 1903, 1019. F.P. 312846, 1901; 317607, 1902; abst. J.S.C.I. 1902, **21**, 134.

atoms, amidines result which are stable to light, and do not develop acidity on standing, due to splitting off of the halogen.[1] They are used in the proportion of about 30 parts to 70 parts of cellulose ester, either with or without alcohol.[2] Those amidines derived from *o*-diamines and not containing halogen, as methenyl-*o*-toluylenediamine, like the toluylenediamines (diamidotoluenes) discolor upon exposure to light, and hence their usefulness is limited to colored or opaque bodies.[3] The same observation applies to methylethenylchloramidine and methenyl-*o*-toluylenediamine, although they possess excellent gelatinizing power.[7] It has been claimed that camphor may be partially replaced with advantage by carboxylic acid derivatives (formyl, acetyl, ethoxyl and benzoyl) of secondary diamines, which are purified by fractional distillation and then by extraction with organic solvents.

1. Badische Anilin & Soda Fabrik, U.S.P. 892899, 1908; abst. J.S.C.I. 1908, **27**, 828. E.P. 10228-A, 1906; abst. J.S.C.I. 1906, **25**, 1064. F.P. 366106, 1906; abst. J.S.C.I. 1906, **25**, 1001; C.A. 1907, **1**, 2960. D.R.P. 180126, 1906; abst. C.A. 1907, **1**, 2203; Chem. Zentr. 1907, I, 1473; Zts. ang. Chem. 1907, **20**, 1541. Cf. E.P. 8077, 10288, 1906.

2. Badische Anilin & Soda Fabrik, E.P. 8077, 1906; abst. J.S.C.I. 1906, 25, 608. First Add. dated May 16, 1906, to F.P. 363846, 1906; abst. J.S.C.I. 1906, **25**, 1064; C.A. 1907, **1**, 2957. D.R.P. 176474, 1905; abst. C.A. 1907, **1**, 1350; Mon. Sci. 1909, (4), **70**, 90; Chem. Zentr. 1907, I, 142; Zts. ang. Chem. 1907, **20**, 369. Belg. P. 191531, 1906.

3. This body, together with o-toluylenemethenylamid, ethylethenyltrichloramid are examples of the general group of amidins derived from o-diamido compounds of the aromatic series, particularly the amidins which can be derived from as-trichlordiamidobenzene and from v-tetrachlordiamidobenzene, which have been patented by C. Schraube and E. Laudien (U.S.P. 892899, 1908; D.R.P. 180126, 1906). They are used in the place of camphor in the ratio of 30 to 100 parts nitrocellulose, alcohol being added as in the regular process of conversion. In U.S.P. 892900, 1908, are given quantitative methods for the manufacture of polychloramidins from as-trichlordiamidobenzene by reducing o-nitroacylamido derivatives (either alphylated or unalphylated) of as-trichlorbenzene or v-tetrachlorbenzene. Methods of producing the following are given in detail; ethenyltrichloramidin, methenyltrichloramidin, ethylethenyltrichloramidin, ethenyltetrachloramidin, benzylethenyltetrachloramidin, benzyltrichloramidin and methylethenyltrichloramidin. Ethenyltrichloramidin is claimed as especially valuable, and preferably obtained by reducing 1-ethylacetylamido-2-nitro-3.4.6-trichlorbenzene, possesses the property of swelling nitrocellulose, melts at 116°, and is readily soluble in hot xylene.

7. Actiengesellschaft f. Anilin Fabrikation, D.R.P. 180216, 1906.

There are a number of substitutes which might constitutionally be applicable, but which gradually split off acid, and therefore slowly induce decomposition of the plastic upon standing. The best known of these derivatives is pinene hydrochloride, which is obtained by passing dry HCl gas through anhydrous turpentine.[1] It resembles natural camphor, and is sometimes confused with the true synthetic camphor. Pinene hydrochloride possesses a low capacity of gelatinization, and in spite of repeated and elaborate purification, splits off HCl in combination with cellulose esters, with decomposition of the latter. *Iso*borneol obtained by the hydration of camphene has many of the desirable properties of camphor, melts at 216°, is soluble in alcohol and sublimes un-decomposed.[2] The principal drawbacks to its extended use are the facts that it is affected by acids and alkalis, and is prone to crystallize from plastic combinations. Borneol[3] is less valuable. Closely related to *iso*borneol is the ester *iso*bornyl acetate,[4] an oil boiling at 285°, resembling camphor chemically, but of low gelatinizing capacity and with a pronounced odor, which to some is repulsive.

The complex and variable products resulting from the treatment of oil of turpentine with sulfuric acid, by mixing it with such products as cymene, terebene, diterebene, colophene, etc., but not nitrocymene or camphene, has a num-

1. E. Callenberg, F.P. 322506, 1902; abst. J.S.C.I. 1903, **22**, 377; Mon. Sci. 1903, (4), **59**, 127. O. Nagel, U.S.P. 596662, 1898, describes the use of "hydrochlorinated turpene."

2. One k!lo of cellulose ester is moistened with a sufficient quantity of 96% ethyl alcohol, and is then mixed with 500 gms. of borneol dissolved in 500-600 gms. ethyl acetate. The mixture is deprived of excess of solvent centrifugally or otherwise.

3. A. Behal, U.S.P. 831028, 1906; abst. C.A. 1907, **1**, 254; J.S.C.I. 1906, **25**, 1064; Mon. Sci. 1907, (4), **67**, 54. E.P. 11512, 1905; abst. J.S.C.I. 1905, **24**, 855. F.P. 349970, 1904; abst. J.S.C.I. 1905, **24**, 984. Belg. P. 184896, 1905. J. Basler & Co., D.R.P. 185808, 1905; abst. C.A. 1908, **2**, 351; J.S.C.I. 1907, **26**, 1064; Zts. ang. Chem. 1907, **20**, 1541; Chem. Zentr. 1907, II, 1037; Jahr. Chem. 1905-08, II, 993. The borneols are first intimately mixed in ether and alcohol with nitrocellulose until dissolved, ethyl acetate, amyl acetate or acetone being added until a homogeneous mass results.

4. C. Claessen, D.R.P. 172941, 1905; abst. Mon. Sci. 1908, (4), **68**, 45; Jahr. Chem. 1905-08, II, 992; Chem. Centr. 1906, II, 736; Zts. ang. Chem. 1907, **20**, 115.

ber of the same drawbacks.[1] Certain tetrasubstituted ureas have been patented by C. Claessen[2] and O. Thieme[3] as gelatinizing media, in which the hydrogen associated with the nitrogen is replaced by organic radicals, but transparent celluloid prepared with them invariably discolors upon long exposure to the light.[4] Those condensation products of hydrochloric acid gas upon benzylidene diaceticester (3-methyl-5 phenyl-4, 6-dicarboxethyl-keto-R-hexen), or obtained from benzaldehyde and acetoacetic ester in the presence of an organic base, are difficult to purify from traces of free acid, and when so purified are prone to split off HCl upon exposure

1. E. Rouxeville, E.P. 13023, 1907; abst. J.S.C.I. 1906, **25**, 83; C.A. 1909, **3**, 83. F.P. 376269, 1906; abst. J.S.C.I. 1907, **26**, 988. Belg. P. 200494, 1907. After treatment of the turpentine in the cold with an equal weight of sulfuric acid, the mixture is allowed to stand and the upper dark layer separated and washed with water. It is gently heated with 50% nitric acid and the resulting brown powder heated with water, washed free from acid and dissolved in acetone. Nitrocotton is then incorporated to a uniform paste, a plastic mass being obtained upon evaporation of the acetone. It is claimed that the addition of resin produces a harder product and linseed oil the converse.

2. C. Claessen, E.P. 20037, 1906; abst. J.S.C.I. 1907, **26**, 112; C.A. 1907, **1**, 945. F.P. 364604, 1906; abst. J.S.C.I. 1906, **25**, 906; C.A. 1907, **1**, 59; Mon. Sci. 1907, (4), **67**, 125. D.R.P. 178133, 1906; abst. C.A. 1907, **1**, 1352; Mon. Sci. 1909, (4), **70**, 90; Jahr. Chem. 1905-08, II, 993; Chem. Zentr. 1907, I, 143; Jahr. Chem. 1905-08, II, 933. Belg. P. 190920, 1906.

3. U.S.P. 831488, 1906; abst. J.S.C.I. 1906, **25**, 1064; C.A. 1907, **1**, 255.

4. W. Lindsay and the Celluloid Co. (U.S.P. 961360, 1910; abst. C.A. 1910, **4**, 2581; J.S.C.I. 1910, **29**, 875. D.R.P. 251372, 1910; abst. Kunst. 1912, **2**, 379, 393; Chem. Zentr. 1912, II, 1248; Zts. ang. Chem. 1912, **25**, 2432. E.P. 13692, 1910; abst. C.A. 1911, **5**, 2925; J.S.C.I. 1911, **30**, 279), have described the use of benzyl benzoate as a camphor substitute in pyroxylin plastic formation, claiming that inodorous moldable products result when the ester is used in the ratio of 20% (calculated on the pyroxylin) for hard compounds, and 150% for very flexible compositions. A few years ago this ester was obtainable only at a prohibitive price for commercial uses, while today it can be prepared from benzaldehyde for about forty cents per pound. The latent solvent action of the cinnamic group of balsams, comprising balsams of tolu, Peru and storax, is undoubtedly due to the benzyl benzoate, benzyl cinnamate, cinnamyl cinnamate (styracin), cinnamyl benzoate and phenylpropyl cinnamate, which together form the major portion of their composition. In this connection see benzyl acetate and ethylenediacetate. E. Seelig (D.R.P. 41507, 1889), benzylmethyl ether, benzylethyl ether; C. Mettler (D.R.P. 166181, 1904; Zts. ang. Chem. 1904, **17**, 1066; Chem. Zentr. 1906, II, 615), benzylaminobenzyl alcohol, monomethylaminobenzyl alcohol and phenylaminobenzyl alcohol; (Kalle & Co.,

to the light.[1] Ethylidenediacetoacetic ester, and benzylideneacetoacetic ester[2] are similar. In 1893 J. Stevens patented the use of acetanilide,[3] and the following year R. Schuepphaus[4] described the advantages of formanilide, *o*-, and *p*-acetphenetidine, *o*- and *p*-acetoluide, brom- and nitro-acetanilide and acettoluides, and benzanilid, which have, in general, proven unsatisfactory except for special uses. With the exception of *sym*-acetyltetrachloraniline and benzylacetylpentachloraniline, the group of alkylated acetyl compounds of those tetra- and higher chlorinated anilines in which both ortho-positions to the amino group are occupied by chlorine, have been very

D.R.P. 97710, 1895).

1. C. Claessen, D.R.P. 172966, 172967, 1904; abst. Mon. Sci. 1908, (4), **68**, 45, 46; Jahr. Chem. 1905-08, II, 992; Zts. ang. Chem. 1907, **20**, 115; Chem. Zentr. 1906, II, 736. F.P. 363090, 1906; abst. J.S.C.I. 1906, **25**, 865; C.A. 1907, **1**, 2956; Mon. Sci. 1907, (4), **67**, 124.

2. C. Claessen, D.R.P. 174259, 1904. Add. to D.R.P. 172966; abst. Jahr. Chem. 1905-08, II, 992; Mon. Sci. 1911, (5), **74**, 63; C.A. 1907, **1**, 1198; Chem. Zentr. 1906, II, 1631; Zts. ang. Chem. 1907, **20**, 115.

3. Chem. Fab. Weiler-Ter-Meer, F.P. 341556, 1904.

4. U.S.P. 528812, 1894; E.P. 21331, 1894; D.R.P. 80776, 1894. Acetanilid is used at the present time to partially replace camphor in pyroxylin plastics, its greatest drawback to more extended use being its difficult solubility in alcohol. However, it is the most valuable (probably) of the inodorous camphor substitutes, and at the same time is comparatively inexpensive. Of more importance at the present time are the substituted acetanilids, patented by Stevens (U.S.P. 551456), in 1895, and since grealy elaborated. Methylacetanilid, sometimes called exalgine, is a colorless, odorless hard crystalline substance, and much more soluble in alcohol than acetanilid. In combination with either camphor or acetanilid, it forms a pyroxylin compound superior to the camphor acetanilid mixture described in J. Stevens, U.S.P. 517987, 1894. Camphor-methylacetanilid mixtures can be manipulated at temperatures below the boiling point of water. Methylacetanilid-phenylacetamide compounds are also easily plastic. The combination of acetanilid, methylacetanilid and alcohol with pyroxylin, produces a readily moldable and, when thoroughly dry, a practically non-shrinkable plastic. Ethylacetanilid, propylacetanilid, butylacetanilid and amylacetanilid, the latter being a liquid, are claimed as efficient camphor substitutes. Ethylacetanilid especially, and its closely allied derivatives, are of great value in forming transparent celluloid sheets. Acet-*p*-phenetidin (*p*-oxyethylacetanilid, phenacetin) formed by acetylizing *p*-amidophenetol, has been patented as a camphor substitute, but appears to have been used principally in pharmacy. U.S.P. 598649, 1898, R. Schuepphaus, comprises acetophenon, benzylidene acetone, benzophenon, phenylbenzyl ketone, oxyacetophenon, benzyl, dibenzylidene acetone, trioxybenzophenon, *p*-oxybenzophenon, oxyphenylbenzyl ketone (benzöin), and trioxyacetophenon (gallacetophenon),

satisfactory,[1] especially *sym*-methylbenzoyltrichloranilide.[2] *Sym*-ethylbenzoyltrichloranilide is less suitable on account of its higher melting point (127-128°). Acetyltrichlor-*o*-phenylenediamine, ethenyltrichloramidine[3] and dihydroxydiphenylsulphone[4] are not odorless. Methyl acetanilide,[5] 4 parts, is claimed to be the equal of camphor 5 parts, when combined with nitrocellulose, 10 parts.

It is well known that useful plastic combinations result from uniting camphor with chloral hydrate, butylchloral hydrate, chloral alcoholate,[6] phenol and its carbonic esters,[7] resins,[8] rosin and naphthalene,[9] resin and castor oil,[10] either with[11]

together with their bromo- and nitro- derivatives. See U.S.P. 410205, 410206, 1889; 528812, 1894.

1. Badische Anilin & Soda Fabrik, F.P. 363846, 1906; abst. C.A. 1907, **1**, 2957. D.R.P. 176474, 1905; abst. C.A. 1907, **1**, 1350; Zts. ang. Chem. 1907, **20**, 369. See also D.R.P. 180208, 1905. F.P. 365297, 1906.

2. Badische Anilin & Soda Fabrik, D.R.P. 180208, 1905; abst. C.A. 1907, **1**, 2204; Chem. Zentr. 1907, I, 1474; Zts. ang. Chem. 1907, **20**, 461.

3. F.P. 366106, 1906; abst. C.A. 1907, **1**, 2960; J.S.C.I. 1906, **25**, 1001. U.S.P. 892899, 1908; abst. J.S.C.I. 1908, **27**, 828. E.P. 10228-A, 1906; abst. J.S.C.I. 1906, **25**, 1064.

4. Chem. Fabrik Griesheim-Elektron, F.P. 404886, 1910; abst. Rev. Chim. Ind. 1910, **21**, 69. D.R.P. 219918, 1908; abst. C.A. 1910, **3**, 827; Chem. Zentr. 1910, I, 1080; Chem. Zts. 1910, **9**, 1932. E.P. 15855, 1909; abst. J.S.C.I. 1909, **28**, 1163.

5. J. Schmerber, F.P. 340266, 1904; abst. J.S.C.I. 1904, **23**, 728.

6. E.P. 9537, 1907; abst. J.S.C.I. 1908, **27**, 589. F.P. 377010, 1907; abst. J.S.C.I. 1907, **26**, 1027; Mon. Sci. 1908, (4), **68**, 444. D.R.P. 189703, 1902; abst. Chem. Zts. 1907, **6**, 387; Chem. Zentr. 1907, II, 1822; Mon. Sci. 1910, (4), **73**, 159. D.R.P. 152111, 1902; abst. Zts. ang. Chem. 1904, **17**, 1250; Chem. Centr. 1904, II, 382; Mon. Sci. 1910, (4), **73**, 159. Jahr. Chem. 1904, 1168. D.R.P. 220228, 1907; abst. Chem. Zts. 1910, **9**, 1934; Chem. Ind. 1910, **33**, 271; Chem. Tech. Rep. 1910, **34**, 180. Aust. P. 34908, 1908; Zts. ang. Chem. 1909, **22**, 505.

7. E. Zuehl, U.S.P. 700884, 1902; abst. J.S.C.I. 1902, **21**, 870. E.P. 17948, 1900; abst. J.S.C.I. 1901, **20**, 926. D.R.P. 139589, 1900; abst. Chem. Centr. 1903, I, 749; Zts. ang. Chem. 1903, **16**, 286; Jahr. Chem. 1903, 1019.

8. J. McClellan, U.S.P. 366231, 1887. Zuehl and Eisenmann, D.R.P. 177778, 1904; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1909, (4), **70**, 90. C.A. 1907, **1**, 1351; Zts. ang. Chem. 1907, **20**, 369. Aust. P. 9557, 13838, 1903.

9. L. Arbezcarme, F.P. 372512, 1906; abst. J.S.C.I. 1907, **26**, 634.

10. C. Gillet, F.P. 352853, 1905; abst. C.A. 1907, **1**, 1497. F.P. 382270, 1906; abst. Mon. Sci. 1909, (4), **70**, 13; J.S.C.I. 1908, **27**, 178. F.P. 352853, 1905; abst. J.S.C.I. 1905, **24**, 984.

or without the addition of stannous chloride. Chloral compounds are precluded on account of their cost, odor and toxicity. The resins tend to induce brittleness. To overcome this tendency, various softeners have been advocated, such as ethyl stearate,[1] methyl, ethyl, propyl or amyl chlorstearates,[2] magnesium, zinc, aluminum and lead ricinoleates,[3] sulforicinoleates [4] and the alkyl ester or esters of the acids obtained by the action of nitric acid upon fats, oils and soaps,[5] but, in the main, they have not been satisfactory. This is especially true of ceresin.[6]

L. Ach and C. Boehringer & Soehne have observed [7] that the property of gelatinizing nitrocellulose is possessed to a large degree by the cyclic acetals, and the condensation products of ketones and aldehydes with polybasic alcohols (pure polyhydroxy compounds of the general formula CH_2OH CHOH $(CH_2OH)x$, where x may be naught. The esters and anhydrides of phthalic, phthalonic, phthalamic and phthalanilic acids, phthalic anhydride and mono-ethyl phthalate;[8]

F.P. 382350, 1906; abst. J.S.C.I. 1908, **27**, 244.

11. S. Assadas, F.P. 387537, 1907; abst. J.S.C.I. 1908, **27**, 873. First Add. dated May 8, 1908, to F.P. 387537.

1. Soc. Anon. Nouvelle "L'Oyonnithe, F.P. 387179, 1908; abst. Mon. Sci. 1909, (4), **70**, 14. J. Goldsmith and British Xylonite Co., D.R.P. 139738, 1901; abst. Mon. Sci. 1904, (4), **60**, 92; Chem. Zentr. 1903, I, 749; Zts. ang. Chem. 1903, **16**, 286.

2. J. Aylesworth, U.S.P. 962877, 1910; abst. C.A. 1910, **4**, 2570. The monoacetyl derivatives of benzidine, tolodine, dianisidine and dichlorbenzidine (J. Cain, J.S.C.I. 1909, **28**, 696), all crystalline, at present are too costly. Benzyl chloride, benzal chloride, chlorbenzol, or benzoyl chloride in the presence of alcohol are feeble solvents of partially hydrated acetated cellulose.

3. A. Peyrusson, F.P. 374395, 1906; abst. J.S.C.I. 1907, **26**, 776.

4. A. Peyrusson, First Add. dated April 13, 1907, to F.P. 374395, 1906.

5. J. Goldsmith and British Xylonite Co., E.P. 22662, 1901; abst. J.S.C.I. 1902, **21**, 1293. D.R.P. 139738, 1904; Jahr. Chem. 1901, 900. Acetated castor oil obtained by treatment of castor oil with acetic acid and acetic anhydride in the presence of a small amount of a condensing medium, is a poor solvent of acetated cellulose, although nitrated castor oil is a solvent of nitrocellulose.

6. C. Claessen, D.R.P. 163668, 1904; abst. Jahr. Chem. 1905-08, II, 992; Chem. Zentr. 1905, II, 1568; Zts. ang. Chem. 1906, **19**, 204.

7. L. Boehringer & Soehne, U.S.P. 996191, 1911; abst. C.A. 1911, **5**, 2743. D.R.P. 214962, 1910; abst. Rev. Chim. Ind. 1910, **21**, 156; Chem. Zentr. 1909, II, 1607.

oxanilic esters, as methyl oxanilate, benzyl oxanilate, and naphthyl oxanilate;[1] naphthyl acetate, naphthyl benzoate;[2] phenyloxyacetic acid, and phenyl and naphthyl naphthoxyacetates[3] are preferably used in conjunction with camphor. Certain aromatic ketones are excellent cellulose ester gelatinizers, such as methylnaphthyl ketone, dinaphthyl ketone, methylhydroxynaphthyl ketone and dihydroxydinaphthyl ketone.[4] preferably dissolved in alcohol.

Naphthalin is difficultly soluble in alcohol[5] and produces odorous plastics, while phenylnapththalin, benzylnaphthalin, dinaphthyl and dinaphthylmethane[6] have no smell. Benzyli-

8. E. Zuehl, E.P. 4326, 1901; abst. J.S.C.I. 1901, **20**, 603. F.P. 308372, 1901; abst. Mon. Sci. 1902, (4), **58**, 159; J.S.C.I. 1902, **21**, 65. First. Add. to F.P. 308372, 1901; abst. Mon. Sci. 1902, (4), **58**, 159; J.S.C.I. 1902, **21**, 65. D.R.P. 127816, 1900; abst. Mon. Sci. 1902, (4), **58**, 78; Chem. Centr. 1902, I, 288; Zts. ang. Chem. 1902, **15**, 114.

1. E. Zuehl, F.P. 309963, 1901; abst. Mon. Sci. 1902, (4), **58**, 171. D.R.P. 128119, 1901; abst. Mon. Sci. 1902, (4), **58**, 163; Jahr. Chem. 1902, 1057; Zts. ang. Chem. 1902, **15**, 114; Chem. Centr. 1902, I, 387.

2. E. Zuehl, E.P. 11751, 1900; abst. J.S.C.I. 1901, **20**, 741. D.R.P. 118052, 1900; abst. Mon. Sci. 1901, (4), **57**, 165; Zts. ang. Chem. 1901, **14**, 296; Chem. Centr. 1901, I, 551; Jahr. Chem. 1901, 900.

3. Zuehl and Eisenmann, D.R.P. 119636, 1900; Chem. Centr. 1901, I, 924; Zts. ang. Chem. 1901, **14**, 448; Mon. Sci. 1901, **57**, 216.

4. E. Zuehl, E.P. 20723, 1900; abst. J.S.C.I. 1901, **20**, 273, D.R.P. 122166, 1900; abst. Zts. ang. Chem. 1901, **14**, 788; J.S.C.I. 1901, **20**, 926; Mon. Sci. 1901, (4), **57**, 292; Chem. Centr. 1901, II, 251. F.P. 305481, 1900; abst. Mon. Sci. 1902, (4), **58**, 21. Add. of Oct. 8, 1900, to F.P. 301703; abst. Mon. Sci. 1902, (4), **58**, 21. For preparation of olefines, transformation of same into alcohol aldehydes as acetaldol, and the use of the latter as a nitrocellulose colloiding agent, see E. I. du Pont de Nemours Powder Co., F.P. 449605, 449606, 449607, 453164, 1913. E.P. 17259, 1911; abst. J.S.C.I. 1909, **32**, 507, 509, 767; Kunst. 1913, **3**, 175, 195; C.A. 1913, **7**, 417, 696, 2683.

5. J. Chaubet, E.P. 13287, 1899; abst. J.S.C.I. 1900, **19**, 552. F.P. 292983; Graph. Beob. **9**, 219; Am. Apoth. Z. **21**, 31; Pharm. Centralh. **41**, 317. Also patented by Soc. Gen. pour la fabr. des Matieres Plastique (D.R.P. 117542, 1899; abst. Mon. Sci. 1901, **57**, 165). See U.S.P. 543197. The Rheinische Gummi- u. Zelluloid Fabrik (D.R.P. 140480, 1902) have patented the following naphthalin derivatives as camphor substitutes which differ from naphthalin in being odorless, and otherwise are as efficient. They are *a*- and *b*-phenylnaphthalin, *a*- and *b*-benzylnaphthalin, *a*- and *b*-dinaphthyl, and *a*- and *b*-naphthylmethane. *a*- and *b*-naphthyl acetate (Zuehl and Eisenmann, D.R.P. 118052, 1900) are also odorless, and have been patented to replace camphor.

6. Rheinische Gummi -und Zelluloid Fabrik, D.R.P. 140480,

dine diacetate,[1] *m*- and *p*-monochlorbenzylidine diacetate, and benzylidene mono-, and di-acetoacetate all melt under 83° and have a peculiar odor. Phenyl formate, propionate, tartrate and citrate all possess the characteristic phenol odor, and at present are but chemical curiosities.[2] Certain carbohydrates, as dextrin,[3] glucose, levulose, lactose, and others,[4] are water soluble, and hence inadmissable for those plastics, which, like collars and cuffs, are exposed to water or to the elements. The polychloranilines and polychloramidines[5]

1902; abst. J.S.C.I. 1903, **22**, 569; Chem. Centr. 1903, I, 906; Zts. ang. Chem. 1903, **16**, 313; Jahr. Chem. 1903, 1019.

1. C. Claessen, D.R.P. 172966, 1904; Chem. Zentr. 1906, II, 736, 1631; Zts. ang. Chem. 1907, **20**, 115; and First Add. 174259, 1904; 173020, 1904; F.P. 363090, 1906; the cellulose nitrate is treated with a solution of 3.5 k. of the benzylidene compound in 10 l. alcohol and the mass rolled at a temperature between 60-90°. In D.R.P. 118052, 1900, Zuehl and Eisenmann replace camphor by *a*- or *b*-naphthylacetate, which is odorless, ethyl alcohol being the solvent. In D.R.P. 119636, 1900, they claim esters of naphthoxylacetic and phenyloxylacetic acids, and submit the following as the desirable combinations: 1.5 k. phenoxylacetic acid with 10 k. nitrocellulose; 3 k. amyl naphthoxylacetate with 6 k. nitrocellulose; 50 k. naphthyl naphthoxylacetate, $C_{10}H_7OCH_2COOC_{10}H_7$ with 100 k. nitrocellulose. See also the celluloid-like masses of C. Claessen, Aust. P. 25335, 27060, 1906.

2. E. Zuehl, E.P. 17948, 1900.

3. D.R.P. 168497, 1903; abst. Zts. ang. Chem. 1906, **19**, 1271; Chem. Zentr. 1906, I, 1388; Wagn. Jahr. 1906, 526.

4. The Rheinische Gummi- und Zelluloid Fabrik (D.R.P. 140858, 1902; abst. Zts. ang. Chem. 1903, **16**, 353; J.S.C.I. 1903, **22**, 569; Chem. Zentr. 1903, I, 741), replace camphor by glucose, levulose and lactose in D.R.P. 168497, 1903; abst. J.S.C.I. 1906, **25**, 775; Mon. Sci. 1908, (4), **68**, 45; Zts. ang. Chem. 1906, **19**, 1271; Chem. Centr. 1906, I, 1388, by sugar and dextrin, and in D.R.P. 140263, 1902; abst. Jahr. Chem. 1903, II, 1019, by acid esters of the above. Those which have been found suitable are, acetochlorhydrose, glucose dibutyrate, glucose distearate, glucose ditartrate, glucose tetratartrate, glucose diacetate, tri-, tetra-, and oct-acetyldiglucose; pentacethyllevulose, tetracetyllactose, lactose tartrate; saccharose mono-, tetra-, hepta- and saccharose octa-acetate.

5. The Badische Anilin und Soda Fabrik have patented (E.P. 10228, 1906; abst. J.S.C.I. 1906, **25**, 866) the use of certain polychlor-anilines and -amidines, as camphor substitutes, giving methods of preparation and melting points of ethenyl-, methenyl-, methylmethenyl-, ethylethenyl-, benzylethenyl-, benzenyl-, and methylmethenyl-trichloramidine; monoethylacetyl-, monomethylacetyl-, ethylbenzoyl-trichloranilid; as methylacetyl-, *s*-benzylacetyl-, benzylbenzoyl-, and *s*-benzylacetyl-tetrachloranilid. Also (D.R.P. 180126, 1906; abst. Zts. ang. Chem. 1907, **20**, 154; Chem. Zentr. 1907, **78**, 1473; Wagn. Jahr. 1907, 562; Chem. Tech. Rep. 1907, **31**, 77), amidines derived from aromatic o-diamines, there being specified methyl-o-toluylene diamine (m. pt., 113-115°); ethylethenyltrichlor-o-phenyl-

have been a fruitful field for special plastic-inducing and gelatinizing cellulose ester bodies, as well as the "Plastol" group of the firm of Meister, Lucius and Bruening.[1] The "acetin" series of J. Goldsmith[2] includes solvents of both

enediamine (m. pt., 116-117°) obtained by the reduction of ethyl-acet-o-nitrochloranilid and methylethenyltrichloramidine (m. pt., 120-121°) obtained by methylating the sodium salt of trichlorethenylamidine.

1. Meister, Lucius und Bruening, E.P. 25434, 1899; abst. J.S.C.I. 1901, **20**, 62. U.S.P. 758335, 1904. D.R.P. 122272, 1899; abst. Zts. ang. Chem. 1901, **14**, 788; Chem. Centr. 1902, **72**, II, 328; Wagn. Jahr. 1901, 609; Mon. Sci. 1901, (4), **57**, 292, have evolved a series of camphor substitutes, in which aromatic sulpho acids of the general type R-SO_2A are used to partially or wholly replace the camphor. In this formula, R represents an aromatic radical or its substitution product—such, for instance, as phenyl, tolyl, xylyl, naphthyl, nitrophenyl, nitrotoyly, alkyloxyphenyl, etc.—and A indicates either an aliphatic or aromatic ether residue, such as oxyalkyl or residue of mono or polyvalent alcohol—for instance, methyl, ethyl, benzyl, cinnamyl alcohols, etc—and oxyalphyl or residue of a monovalent or polyvalent phenol, such as phenol, naphthol, cresol, resorcinol, dioxydiphenylmethane, etc., or amido group, which, non-substituted, may be substituted once or twice. This is an exceedingly important group known under the general name of Plastol. The members constituting it are of more interest at the present time than when they were patented, due to the fact that several have been found to be latent solvents of acetylhydrocelluloses and acetyloxycelluloses. The most important of this group are as follows: benzenesulphamid, *p*-toluenesulfamid, *p*-chlorsulphamid, benzenesulfoethylamid, benzene sulfdiethylamid, *p*-toluenesulphoethylamid, *p*-toluenesulfodiethylamid, acetbenzenesulfoamid, acet-*p*-toluenesulfamid, benzenesulfanilid, *p*-chlorbenzenesulfanilid, dibenzyl-*p*-chlorzenesulfamid, dibenzyl-*p*-toluenesulfamid, dibenzyl-*p*-toluenesulfoimid, benzenesulfanilid, *p*-chlorbenzene sulfanilid, dibenzyl-*p*-chlorbenzenesulfanilid, *p*-toluenesulfoanilid, dibenzyl-*p*-toluenesulfoanilid. Benzenesulfo-methylanilid, -ethylanilid, -*o*-toluid, -*o*-chloranilid, -*o*-phenetidin, -*p*-phenetidin, -*a*-naphthylamin, -*b*-naphthylamin and benzenesulfodiphenylamin, *p*-toluenesulpho-methylanilid,-ethylanilid, -*o*-toluid, -*p*-toluid, -*m*-xylidid, -*p*-chloranilid, -*o*-phenetidin, -*p*-phenetidin, -*a*-naphthylamin, -*b*-naphthylamin, -diphenylamin, -phenylhydrazin, -acidphenylether, -cresol, -*b*-naphthol, -*a*-naphthol, -acidethylester. Benzenesulfo-acidphenylether, -*p*-cresol, -*b*-naphthol; dibenzenesulfo-2.7-dioxynaphthalin, *p*-chlorbenzenesulfo-*b*-naphthol, di-*p*-sulfo-2.7-dioxynaphthalin, *p*-chlorbenzenesulfanilid, *p*-toluenesulfamido acetic acid, *p*-toluenesulfamido ethyl ester; *o*-, *p*-, *m*-amidosulfbenzoic acid; *o*-, *p*-, *m*-sulfamidoethylester. The melting points of these sixty-three compounds are within the range of pyroxylin decomposition with but few exceptions, and the melting point may be materially lowered in a number of instances by mixing two or more in various proportions, as for instance, a mixture of *p*-toluenesulfamid (m. pt. 137°) and *p*-toluenesulfomonoethylamid (m. pt. 58°) gives a series of melting points at any degree between these two extremes.

2. J. N. Goldsmith (E.P. 13131, 1900), proposed acetin or any

acetyl- and nitro-cellulose. The camphor substitutes investigated by J. Stevens, dinitrotoluol,[1] naphthalene,[2] dinitroxylol,[3] *p*-nitrotoluol,[4] camphene hydrochloride,[5] the acetxylids,[6] crystalline pyrazolone derivatives,[7] dimethylhydroquinone, thymoquinone, thymol[8] and benzoylguaiacol,[9] all have a lower melting point than camphor. So also salol, betol,[10] naphthol benzoate (benzonaphthol), salacetol and benzoic anhydride and methyl, ethyl, propyl, butyl and amyl carbanilates.[11] Continuing his researches, there was included the crystalline toluol chlorides and benzyl nitrochlorides[12] and the crystalline chlorides, bromides, nitrochlorides and nitrobromides of benzene and their relative efficiency as adjuncts to camphor made known. Alkyl citrates,[13] carbonates[14] and specific crystalline organic sulfur compounds[15] were found to possess distinct advantages for special effects.

Cyclohexanone, cyclohexanol, methyl-cyclohexanol (hexahydro-*o*-cresol), *l*-methyl-cyclohexanone[16] have agreeable

acetic esters of glycerol, acetochlorhydrin, benzicin or the benzoic esters of glycerol, methyl, ethyl, propyl, butyl and amyl phthalates and succinates, pulegone as found in oil of pennyroyal, thujone as obtained from thuja oil, and although it is admitted they are more costly than camphor, a lower volatility and greater solvent efficiency is claimed. See E. Zuehl, E.P. 10213, 1901; F.P. 310942, 1901; abst. Mon. Sci. 1902, (4), **58**, 174; Weiler Ter Meer, E.P. 16271, 1906; Gum. Ztg. 1908, **23**, 20, gives resume of camphor substitutes patented.

1. U.S.P. 542692, 1895.
2. U.S.P. 543198, 1895.
3. U.S.P. 553270, 1896.
4. U.S.P. 552209, 1895
5. U.S.P. 552934, 1895.
6. U.S.P. 564343, 1895.
7. U.S.P. 566349, 1895.
8. U.S.P. 607554, 1898.
9. U.S.P. 572134, 1896.
10. U.S.P. 568104, 1890.
11. The solvent property of these urethanes decreases with increase in molecular weight.
12. U.S.P. 568105, 1896.
13. U.S.P. 583516, 1897.
14. U.S.P. 568106, 1896.
15. U.S.P. 572135, 1896.
16. F. Raschig, U.S.P. 900204, 1908; abst. J.S.C.I. 1908, **27**, 1082; C.A. 1909, **3**, 596. D.R.P. 174914, 1905; abst. J.S.C.I. 1907, **26**, 340; C.A. 1907, **1**, 1198; Mon. Sci. 1911, (5), **74**, 63; Zts. ang. Chem. 1907, **20**, 369; Chem. Centr. 1906, II, 1702; Chem. Zts. 1907, **6**, 9; Wagn. Jahr. 1906, 527; Chem. Tech. Rep. 1906, **30**, 346.

mint-like odors, are excellent solvents and possess a high power of gelatinization. The same is true of some of their esters, especially [1] cyclohexanol formate and acetate, cyclopentanol acetate, *b*-methylcyclopentanol acetate, *o*-methylcyclohexanol formate. Tetrasubstituted ureas as *as*-diethyldiphenylurea, 5-diethyldiphenylurea and tetraphenylurea combine power of gelatinization with being useful antacids.[2] Maisin, a protein substance obtained from maize by amyl alcohol extraction,[3] acetdiphenylamine,[4] hydrobenzylketones, hydronaphthylketones,[5] non-polymerized aldols as acetaldol,[6] *p*-nitroacetoacetanilide,[7] cyclohexanol acetate,[8] formylated albumen,[9] nitronaphthalin,[10] dichlornitronaphthalin with trichloraniline [11] have also been claimed as efficient.

While many of the above named compounds may be unsuitable in combination with acetylcellulose, some chemist may discover a combination which may impart a lasting plasticity of the cellulose formates and acetates, and in this possibility lies the value of the above enumeration.

1. Badische Anilin und Soda Fabrik, E.P. 3869, 1912; abst. Kunst. 1913, **3**, 94; C.A. 1913, **7**, 2683.

2. C. Claessen, E.P. 20037, 1906; abst. J.S.C.I. 1907, **26**, 112. D.R.P. 178133, 1906; Chem. Zentr. 1907, I, 143.

3. E. Donard and H. Labbe, Compt. rend. 1902, **135**, 744; abst. J.S.C.I. 1902, **21**, 1464; Compt. rend. 1903, **137**, 264; abst. J.S.C.I. 1903, **22**, 960. F.P. 320027, 1902. First Add. dated Nov. 3. 1902. Second Add. dated Jan. 5, 1905; abst. J.S.C.I. 1902, **21**, 1548; 1903, **22**, 816; 1905, **24**, 853. F.P. 388097, 1908; abst. J.S.C.I. 1908, **27**, 873. D.R.P. 251259, 262092, 1912; abst. C.A. 1913, **7**, 252, 3444.

4. Deutsche Zelluloid Fabrik, F.P. 312086, 1901; abst. Mon. Sci. 1902, (4), **58**, 194. D.R.P. 132371, 1901; abst. Zts. ang. Chem. 1902, **15**, 720; Wagn. Jahr. 1902, 594.

5. P. Bretau and H. Leroux, F.P. 409557, 1910.

6. E. du Pont de Nemours Powder Co., F.P. 449606, 1912; abst. C.A. 1913, **7**, 2683.

7. D.R.P. 246382, 1911; abst. J.S.C.I. 1912, **31**, 605; Chem. Zentr. 1912, I, 1677; Zts. ang. Chem. 1912, **25**, 1151; Chem. Tech. Rep. 1912, **36**, 304.

8. O. Schmidt, G. Lutz, and T. Eichler, U.S.P. 1045895, 1913; abst. C.A. 1913, **7**, 712.

9. Societe anonyme L'Oyonnaxienne, F.P. 331819, 1903; abst. Mon. Sci. 1904, (4), **60**, 69.

10. Societe Neumann, Marx et Desvaux, F.P. 300672, 1900; abst. Mon. Sci. 1901, (4), **57**, 60.

11. E. Zuehl, F.P. 310942, 1901; abst. Mon. Sci. 1902, (4), **58**, 174.

Diacetone Alcohol.[1] (4-hydroxy-2-keto-4-methylpentan, diacetonyl alcohol) may be prepared by treatment of diacetonamin with nitrous acid,[2] by treatment of raw acetone with caustic potash solution (sp. gr. 1.25-1.3) and distilling off the unchanged acetone.[3] Two recent processes have been patented for its manufacture by A. Hoffmann [4] and by W. Doerflinger.[5] In the first method, acetone in the liquid form is passed over a catalytic agent as slaked lime in granular or powdered condition, the mixture of diacetonyl alcohol and acetone being then neutralized and fractionated, acetone being again led over the catalytic agent. In the second process, the acetone is treated with an alkaline condensing agent at the ordinary temperature in the presence of an inert organic liquid which dissolves the condensing agent and is at the same time soluble in acetone, e. g. an alkali hydroxide in the presence of an aliphatic alcohol as wood alcohol being used. Under the name of "Alco Deo" it is understood this solvent is manufactured in considerable quantities by the Hoffmann method, by a firm near Passaic, New Jersey.

Diacetone alcohol is a colorless, mobile liquid, when

1. For more complete statement of the properties and solvent uses of diacetone alcohol, see Part Two of this work.

2. W. Heintz, Ann. 1875, **178**, 342; Chem. Centr. 1875, 805; Jahr. Chem. 1875, 281; Bull. Soc. Chim. 1876, (2), **26**, 412; J.C.S. 1876, **30**, 1, 375.

3. W. Heintz, Ann. 1873, **169**, 114; abst. Chem. Centr. 1873, 79; Jahr. Chem. 1873, 481; Bull. Soc. Chim. 1874, **21**, 452; J.C.S. 1874, **27**, 145.

4. D.R.P. 229678, 1909; abst. J.S.C.I. 1910, **30**, 307; C.A. 1911, **5**, 2535; abst. Chem. Zentr. 1911, I, 275; Jahr. Chem. 1909, 326; Zts. ang. Chem. 1911, **24**, 190; Chem. Ind. 1911, **34**, 82; Chem. Tech. Rep. 1911, **35**, 40. U.S.P. 1082424, 1913; abst. C.A. 1914, **8**, 788; J.S.C.I. 1914, **33**, 103; Mon. Sci. 1914, 66.

5. U.S.P. 1066474, 1913; abst. J.S.C.I. 1913, **32**, 806; C.A. 1913, **7**, 2994. An apparatus has recently (U.S.P. 1075284, 1913; abst. C.A. 1913, **7**, 4046; J.S.C.I. 1913, **32**, 1030) been patented by C. Crockett for the continuous manufacture of diacetone alcohol. The plant consists of a reservoir for acetone, connected with a "converter tank" containing an insoluble, granular catalytic agent, which will partially polymerise the acetone. The liquid is then passed successively through a series of evaporating units each kept at the same temperature; in these evaporators some of the unpolymerised acetone is driven off, and the liquid becomes progressively richer in diacetone-alcohol, which is finally condensed after leaving the last evaporating unit. A condenser for the unconverted acetone is provided, and is connected with the acetone reservoir in such a manner that the unconverted acetone may be returned for further treatment.

pure of sp. gr. 0.9306 at 25°. The commercial article has a sp. gr. of 0.91-0.925, depending upon the amount of unchanged acetone contained therein. That is, the higher the sp. gr. of commercial diacetone alcohol, the less acetone it contains. It is miscible with water, alcohol, acetone, chloroform, acetylene tetrachloride and amyl acetate without turbidity, is an excellent solvent of nitrated cellulose and acetone-soluble acetylcellulose, but is a poor solvent of castor oil and other vegetable and animal oils. Boiling point, 163.5-164.5°. It is not generally miscible with benzine, but is miscible with benzol, which is its proper diluent. Cellulose esters used with diacetone alcohol should be strictly neutral, for a trace of acid causes the solution to rapidly discolor. On account of the high boiling point, this solvent forms a valuable constituent in acetylcellulose lacquers, Doerflinger having patented its use in this connection.[1] George H. Stevens in his investigation upon cellulose ester solvents and miscible combinations has found that diacetone alcohol in conjunction with toluene, acetone, shellac and acetylcellulose, produces an excellent lacquer for the protection of wood and metal surfaces, which is practically nonhygroscopic, and distinctly thermoplastic.

Solvent Recovery. A. Wohl[2] in recovering volatile solvents from cellulose ester solutions, differs from the usual method of washing the air charged vapors with heavy, volatile absorptive liquids and driving off the solvents by fractionation, in leading the vapors over dry cellulose esters, whereby they are retained by absorption. In other methods, refrigeration with brine or ammonia is resorted to, the deposited solvents being freed from moisture by dehydration and further purified by distillation.

1. U.S.P. 1008438, 1911; abst. J.S.C.I. 1911, **30**, 1398; C.A. 1912, **6**, 183. E.P. 11728, 1911; abst. J.S.C.I. 1911, **30**, 1447. F.P. 429754, 1911; abst. J.S.C.I. 1911, **30**, 1398. D.R.P. 246967, 1910; abst. Chem. Zentr. 1912, I, 1938; Chem. Ind. 1912, **35**, 356; Chem. Tech. Rep. 1912, **36**, 332; Zts. ang. Chem. 1912, **25**, 1550; Mon. Sci. 1912, **77**, 160; Wagn. Jahr. 1912, II, 603. Can. P. 136538, 1911; abst. C.A. 1912, **6**, 303.

2. E.P. 23995, 1911; abst. J.S.C.I. 1912, **31**, 279. D.R.P. 241973, 1910; abst. J.S.C.I. 1912, **31**, 225; Chem. Zentr. 1912, **83**, 307; Wagn. Jahr. 1911, II, 422; Chem. Ind. 1912, **35**, 57; Zts. ang. Chem. 1912, **25**, 286; C.A. 1912, **6**, 2170; Chem. Tech. Rep. 1912,

Wood Oil,[1] a volatile liquid of varying and uncertain composition obtained from the distillation of wood, is, after purification, an excellent solvent for those forms of cellulose acetate which also dissolve in acetone. In the original and crude state it has a very pronounced and pungent odor, attacking the mucous membrane of both eyes and nose. The oil may be purified by neutralization with aqueous sodium carbonate, distillation with hydrochloric acid, neutralization of acid distillate and fractionation to render anhydrous. Thus prepared, a yield of about 65% of the crude is obtained, the rectified oil being miscible with alcohol, ether, fusel oil, amyl acetate, acetone, acetylene tetrachloride and chloroform, and, when sufficiently anhydrous, miscible without turbidity with benzine. benzene or carbon tetrachloride. The rectified oil boils at 65-125°, is insoluble in water, not hygroscopic, an excellent solvent of shellac, dammar, sandarac, the softer copals and mastic, and will dissolve a wide range of partially hydrated acetated celluloses.

Hydrocarbon Chlorides.[2] Various substituted chlorine derivatives of methane, ethane, ethylene and acetylene have proven valuable solvents, plastic-inducing bodies and diluents in the cellulose acetate industry, either alone or associated with other liquids of inhibitive or dissolving power. They combine relatively low inflammability, a wide range of boiling points and speed of evaporation, are non-hygroscopic and water-insoluble, and can be regained unchanged by simple distillation. Inasmuch as but little information on these solvents is to be found in English, as it appears that their usefulness is but, as yet, imperfectly recognized, they are discussed somewhat in detail herewith.

36, 49; Chem. Zts. 1912, 11, 2801. Belg. P. 241116, 1911. Aust. P. 29b, A-9229-11; Kunst. 1912, 2, 340. Hung. Anm. W.-2976; W-3204, 1911.

1. For comprehensive article on composition of wood oil, see G. Fraps, Am. Chem. J. 1901, 25, 27; abst. J.S.C.I. 1901, 20, 237; J.C.S. 1901, 80, I. 188; Chem. Zentr. 1901, I, 439; Jahr. Chem. 1901, 566; Bull. Soc. Chim. 1901, (3), 26, 439.

2. For the physical constants of some chlorinated hydrocarbons, see W. Herz and W. Rathmann, Chem. Ztg. 1913, 37, 621; Zts. Elektroch. 1913, 19, 887; abst. C.A. 1913, 7, 3866; J.S.C.I. 1913, 32, 1128. For the b. pt., freezing pt., sp. gr., coefficient of expansion, heat of vaporization, refractive index, specific heat, and solvent

The Akt.Ges f. Anilin-Fabrikation[1] manufacture non-inflammable solutions of the cellulose nitrates, especially suitable for lacquers, by adding large proportions of di-, tri- or tetrachlorethylene, or tetrachlorethane to a concentrated pyroxylin solution.

Chloroform (Trichlormethane), in the earlier days of the cellulose acetate art, was the most important and widely used solvent. Before partial hydration after acetation was commercially practiced, the normal triacetate was most often used for films and sheets, and for this, chloroform was found to be most satisfactory, although the art was necessarily restricted on account of the cost of chloroform, and its high specific gravity, which made the cost of solutions in bulk correspondingly more expensive. Chloroform is a solvent for the yellowish, hard and horny not-hydrated cellulose acetate, and does not dissolve that form of acetate which is completely soluble in 99% acetone or better. However, the addition of 5-15% of ethyl alcohol to the chloroform will greatly increase the range of solubility of the latter for cellulose acetates, so that acetone-soluble esters may also completely dissolve in a mixture of 85% chloroform and 15% alcohol (each by weight). Many discrepancies are to be found in the literature and works of reference as to the solubility of cellulose acetate in chloroform. Pharmacopeal chloroform has intentionally added to it as a preservative, a small amount of alcohol, so that chloroform of Pharmacopeal purity does not indicate a 100% product. The introduction of as small amount as 2% of alcohol into chloroform will materially modify its dissolving action upon acetylcellulose, especially if the latter has been hydrated close to that point represented by insolubility in chloroform and solubility in absolute acetone. This probably in a great measure accounts for the want of concordance in published statements of the solubility of non-inflammable esters in chloroform. Those cellulose acetates which dissolve

action of 248 organic substances and 45 dyestuffs upon the chlorohydrocarbon solvents ranging from *cis*-dichlorethylene (b. pt. 48.8°) to hexachlorethane (b. pt. 185.5°), see L. Gowing-Scopes, Anal. 1914, **39**, 4; abst. J.S.C.I. 1914, **33**, 160.

1. F.P. 461034, 1913; abst. J.S.C.I. 1914, **33**, 93.

in chloroform do not form flexible films of maximum strength, and hence, as a cellulose ester solvent, chloroform is little, if ever, used at the present time, but has given way to the chemically allied body, tetrachlorethane.

The processes of the Actiengesellschaft f. Anilin-Fabrikation,[1] Balston and Briggs,[2] C. Cross,[3] F. Bayer and Co.,[4] all result in the formation of cellulose esters entirely soluble in chloroform. Pentachlorethane added to chloroform increases the solvent power of the latter.[5] The process of F. Bume [6] for the formation of celluloid substitutes from acetylcellulose, chloroform and camphor has not been a commercial success.

Carbon Tetrachloride (Benzinum, Benzinoform, Detergine, Katharin, Phoenixin, Benzum, Carbona),[8] is a colorless,

1. E.P. 14255, 1906; abst. J.S.C.I. 1907, **26**, 220; C.A. 1907, **1**, 1341. F.P. 368738, 1906; abst. J.S.C.I. 1907, **26**, 30. D.R.P. 198482, 1905; abst. Mon. Sci. 1911, (5), **74**, 54; Zts. ang. Chem. 1908, **21**, 1760; Chem. Zentr. 1908, II, 118; Chem. Ind. 1908, **31**, 378; Jahr. Chem. 1905-08, II, 982.

2. E.P. 10243, 1903; abst. J.S.C.I. 1904, **23**, 557.

3. U.S.P. 530826, 1894. E.P. 9676, 1894; abst. J.S.C.I. 1895, **14**, 496, 987; Amateur Photog (London), 1899, **30**, 146; Brit. Jour. Photog. 1899, 771; Chem. Centr. 1896, I, 405. D.R.P. 85329, 1894; abst. Chem. Centr. 1896, I, 1119; II, 567; Mon. Sci. 1900, (4), **55**, 134; Wagn. Jahr. 1896, **42**, 684; Ber. 1896, **29**, 312; Jahr. Chem. 1896, 1030. D.R.P. 86368, 1895, Add. to D.R.P. 85329; abst. Chem. Centr. 1906, II, 567. F.P. 243546, 1894. Belg. P. 113156, 1894.

4. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, (4), **60**, 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904. 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 780. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, (4), **60**, 54. Aust. P. 31391. It. P. 62042, 1901.

5. E.P. 14364, 1910; abst. J.S.C.I. 1910, **29**, 1152. D.R. Anm. F.-28111, of Aug. 25, 1909; refused Feb. 20, 1911. Aust. P. 46991, 1910. Swiss. P. 52438; abst. Kunst. 1912, **2**, 135. F.P. 417250, 1910; abst. J.S.C.I. 1911, **30**, 19; Mon. Sci. 1913, **78**, 30.

7. E.P. 19735, 1908; abst. J.S.C.I. 1910, **29**, 18. F.P. 393963, 1908; abst. J.S.C.I. 1909, **28**, 257. D.R.P. 223793, 1907; Add. to D.R.P. 210519. Aust. P. 51094, 1908.

8. For general articles upon the manufacture and applications of carbon tetrachloride, see J. Crocker, Electrochem. Met. Ind. 1907, **5**, 259; abst. C.A. 1907, **1**, 2361. E. Graefe, Chem. Rev. Fett. u. Harz., Ind. 1906, **13**, 30-32; abst. Jahr. Chem. 1905-08, II, 138; Chem. Zentr. 1908, I, 874; II, 1411; Chem. Tech. Rep. 1906, **30**, 69; Zts. ang. Chem. 1906, **19**, 202. E. F. Cote, Mon. Sci. 1908, **69**, (4), 22, 677; abst. Jahr. Chem. 1905-08, II, 138; C.A. 1909, **3**, 1398.

highly refractive, ethereal smelling liquid, boils at 78.1°, possesses a sp. gr. of 1.63,[1] a low specific heat (0.219 at 80°), a low latent heat of evaporation, and is practically insoluble in water.[2] It is a non-solvent in all forms of cellulose acetate, which is remarkable, considering the excellent dissolving power, of chloroform, acetylene, tetrachloride, and the chlorhydrins, which are so nearly related chemically.

Carbon tetrachloride may be produced by acting on carbon with the vapors SCl_2 in admixture with an excess of chlorine at a temperature above 900°[3] by saturating carbon tetrachloride and SCl_2 with carbonsulfide;[4] or in presence of

C. Baskerville and H. S. Riederer, J. Ind. Eng. Chem. 1912, **4**, 645; abst. J.S.C.I. 1912, **31**, 934; Kunst. 1913, **3**, 353. Utz, Schweiz. Wochenschr. Chem. Pharm., **48**, 209; abst. Jahr. Chem. 1905-08, II, 139. H. Pichon and T. Truchelut, F.P. 402235, 1909; abst. J.S.C.I. 1909, **28**, 1273; C.A. 1911, **5**, 974. Paraf-Javal, F.P. 327969, 1902; abst. J.S.C.I. 1903, **22**, 1014; Chem. Ztg. 1907, **31**, 326; abst. C.A. 1907, **1**, 1779.

1. S. Young, Sc. Proc. R. Dub. Soc. (N.S.), 1910, **12**, 427, gives the following density results: Temperature 10 deg., equal to 1.6132; 20 deg., equal to 1.5939; 30 deg., equal to 1.5748; 40 deg., equal to 1.5557; 50 deg., equal to 1.5361; 60 deg., equal to 1.5165; 70 deg., equal to 1.4963; 80 deg., equal to 1.4765; 90 deg., equal to 1.4554; 100 deg., equal to 1.4343. Other density results are: 23.13°/4°, equal to 1.58725 (D. Tyrer, J.C.S. 1912, **101**, 84; abst. Chem. Zentr. 1912, I, 975; Bull. Soc. Chim. 1912, (4), **12**, 1032); 20°/4°, equal to 1.5930 (H. Malosse, Compt. rend. 1912, **154**, 1697; abst. Chem. Zentr. 1912, II, 600; Bull. Soc. Chim. 1912, (4), **11**, 309; J.C.S. 1912, **102**, i, 636; C.A. 1912, **6**, 2351; J.S.C.I. 1912, **31**, 701); 0°/4°, equal to 1.63255 (J. Timmermans, Sc. Proc. R. Dub. Soc. 1912, **13**, 326; Bull. Soc. Belg. 1912, **26**, 207; abst. Chem. Zentr. 1912, II, 1712); 0°/4°, equal to 1.63202 (T. Hill, J.C.S. 1912, **101**, 2467; abst. Chem. Zentr. 1913, I, 1401; C.A. 1913, **7**, 1318); 15°/4°, equal to 1.6011; 25°/4°, equal to 1.5835; 35°/4°, equal to 1.5647; 45°/4°, equal to 1.5459; 60°/4°, equal to 1.5172 (W. Herz and W. Rathman, Chem. Ztg. 1912, **36**, 1417; abst. Chem. Zentr. 1913, I, 229; J.C.S. 1913, **104**, i, 695; ii, 26; C.A. 1913, **7**, 1318, 3866.

2. According to Rex, Zts. Phys. Chem. 1906, **55**, 355, the solubility of carbon tetrachloride in 100 gm. water is as follows: Temp. 0 deg. is equal to 0.097; 10 deg. is equal to 0.083; 20 deg. is equal to 0.080; 30 deg. is equal to 0.085 gm. For examination of carbon tetrachloride, see L. Radcliffe, J.S.C.I. 1909, **28**, 229; abst. J.C.S. 1909, **96**, ii, 438.

3. A. and P. Combes, D.R.P. 204942, 1904; abst. C.A. 1909, **3**, 1450. See also A. Henning and E. Bruehl, E.P. 7259, 1912; abst. J.S.C.I. 1913, **32**, 252. J. MacKaye, U.S.P. 880900, 1908; abst. J.S.C.I. 1908, **27**, 356.

4. W. Doerflinger, U.S.P. 992551, 1911; abst. J.S.C.I. 1911, **30**, 768; Chem. Tech. Rep. 1911, **35**, 435.

aluminum amalgam,[1] or aluminum chloride;[2] by heating sulfur chlorides in a vertical retort;[3] by heating calcium chloride and carbon in suitable proportions to a high temperature in an electric current in presence of a non-oxidizing gas;[4] or by passing chlorine through carbon disulfide into SCl_2 containing antimony chloride.[5] J. Febvre,[6] and E. Cote and P. Pierron,[7] have devised a process for its continuous production. The crude chloride is usually contaminated with carbon disulfide, sulfur chloride and free chlorine. These impurities may be removed by preliminary distillation and treatment with hot alkaline carbonate solution,[8] by digestion with an alkali or alkaline earth sulfide,[9] or by treatment at 35° with hypochlorous acid and distilling off the pure carbon tetrachloride.[10]

In the cellulose ester industry the use of carbon tetrachloride has been confined to acetating[11] or nitrating[12] in

1. J. Danziger, U.S.P. 794789, 1905; abst. J.S.C.I. 1905, 24, 903.

2. A. Urbain, Rev. Prod. Chim. 4, (15), 228; abst. J.S.C.I. 1901, 20, 1232. E.P. 13733, 1901; abst. J.S.C.I. 1902, 21, 926. See also F. Machalske, U.S.P. 808100, 1905; abst. J.S.C.I. 1906, 25, 559. Belg. P. 177234, 177235, 177236, 1904.

3. C. Combes, E.P. 25688. 1901; abst. J.S.C.I. 1902, 21, 1469. U.S.P. 735948, 1903; abst. J.S.C.I. 1903, 22, 1013. F.P. 312046, 1901; abst. J.S.C.I. 1902, 21, 1469. First Add. dated Aug. 18, 1904, to F.P. 312046, 1901; abst. J.S.C.I. 1905, 24, 1188. See also F. Maywald, U.S.P. 870518, 1907; abst. J.S.C.I. 1907, 26, 1253; J. MacKaye, U.S.P. 1009428; abst. C.A. 1912, 6, 1275.

4. J. Matthews, U.S.P. 835307, 1906; abst. J.S.C.I. 1906, 25, 1232; C.A. 1907, 1, 499.

5. E. Haworth and H. Baker, E.P. 9404, 1905; abst. J.S.C.I. 1906, 25, 559.

6. J. Febvre, F.P. 355423, 1905; abst. J.S.C.I. 1905, 24, 1189.

7. E. Cote and P. Pierron, F.P. 327322, 1902; abst. J.S.C.I. 1903, 22, 962.

8. E. Cote, F.P. 357781, 1905; abst. J.S.C.I. 1906, 25, 134; C.A. 1907, 1, 665.

9. J. Danziger, U.S.P. 794970, 1905; abst. J.S.C.I. 1905, 24, 903.

10. C. Acker, U.S.P. 875232, 1907; abst. J.S.C.I. 1908, 27, 182; Chem. Tech. Rep. 1908, 32, 71. See also Soc. Anon. d'Etudes Electro-chimiques, F.P. 320269, 1902; abst. J.S.C.I. 1903, 22, 100.

11. C. Dreyfus, F.P. 430606, 1911; abst. J.S.C.I. 1911, 30, 1375. L. Lederer, U.S.P. 999236, 1911; abst. J.S.C.I. 1911, 30, 1050. E.P. 3103, 1907; abst. J.S.C.I. 1907, 26, 889. F.P. 374370, 1907; abst. J.S.C.I. 1907, 26, 776; Mon. Sci. 1908, (4), 68, 84; Chem. Zts. 1907, 6, 139. E.P. 11749, 1900; abst. J.S.C.I. 1901, 20, 741. D.R.P. 163316, 1901; abst. Jahr. Chem. 1905-08, 984; Chem. Ind. 1905, 28, 659; Zts. ang. Chem. 1906, 19, 204; Chem. Centr. 1905, II, 1301; Mon. Sci. 1906, (4), 64, 159. D.R.P. 200916, 1901, add to D.R.P. 163316, 1901; abst. Zts. ang. Chem. 1908, 21, 2047; Chem. Zentr.

which the tetrachloride has been used as a diluent, or as a precipitant.[1] It has but little action upon cast iron.[2] Other uses of carbon tetrachloride are as a fire extinguisher,[3] insecticide,[4] cleansing product,[5] as an emulsifier in petroleum soaps[6] and as a solvent of resins[7] waxes,[8] bitumens,[9]

1908, **79**, 738; Chem. Ind. 1908, **31**, 559; Mon. Sci. 1911, (5), **74**, 82. F.P. 319848, 1902; abst. J.S.C.I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **60**, 123. Aust. P. 42440, 1909. L. Lederer, U.S.P. 902093, 1908; abst. J.S.C.I. 1908, **27**, 1130. E.P. 26501, 1906; abst. J.S.C.I. 1907, **26**, 430. F.P. 371356, 1906; J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 79. D.R.P. 185151, 1905; abst. Zts. ang. Chem. 1907, **20**, 154; Chem. Zentr. 1907, **78**, 498; Jahr. Chem. 1905-08, I, 984. See also D.R. Anm. D.-23457, 1910; D.-29692, 1913; abst. Kunst. 1914, **4**, 20.

12. L. Lederer, U.S.P. 1028748, 1912; abst. J.S.C.I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164. F.P. 368766, 1906; abst. J.S.C.I. 1907, **26**, 30. E.P. 19107, 1906; abst. J.S.C.I. 1907, **26**, 220. F.P. 402072, 1909; abst. Mon. Sci. 1911, (5), **74**, 153. D.R.P. 179947, 1905; abst. C.A. 1907, **1**, 1507; J.S.C.I. 1907, **26**, 889; Zts. ang. Chem. 1907, **20**, 1194; Mon. Sci. 1909, (4), **70**, 68; Jahr. Chem. 1905-08, II, 986; Chem. Zentr. 1907, [(5), **11**], 433; Wagn. Jahr. 1907, I, 419. D.R.P. 200149, 1905, being Add. to D.R.P. 179947, 1905; abst. Jahr. Chem. 1905-08, II, 986;Chem. Zentr. 1908, **79**, 551; Zts. ang. Chem. 1908, **21**, 2047. D.R.P. 210778, 1906; abst. Chem. Zentr. 1909, **80**, 247; Chem. Zts. 1909, **8**, 1474; Zts. ang. Chem. 1909, **22**, 1620; Chem. Ind. 1909, **32**, 383.

1. Soc. Anon. d'Explosifs et de Produits Chimiques, F.P. 385179, 1907; abst. Mon. Sci. 1909, (4), **70**, 105; Bull. Soc. Chim. 1909, (4), **6**, 557; C.A. 1909, **3**, 2383. F.P. 385180, 1907; abst. J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 106; Bull. Soc. Chim. 1909, (4), **6**, 557.

2. R. Bolis, Chem. Ztg. 1906, **30**, 1117; abst. J.S.C.I. 1906, **25**, 1159.

3. E. Davidson, U.S.P. 1010869, 1911; 1036461, 1912; abst. J.S.C.I. 1912, **31**, 860. F.P. 428315, 1911; abst. J.S.C.I. 1911, **30**, 1149. E.P. 12233, 1910; abst. J.S.C.I. 1911, **30**, 272. E.P. 3704, 1909; abst J.S.C.I. 1909, **28**, 829. J. Robinson, Eng. News, **65**, 326.

4. M. Porter, U.S.P. 1010797, 1911.

5. C. Nowak, U.S.P. 1038783, 1912; abst. J.S.C.I. 1912, **31**, 997; C.A. 1912, **6**, 3498. P. Surcouf, F.P. 392504, 1907; abst. J.S.C.I. 1908, **27**, 1201. J. Stockhausen, U.S.P. 845322, 1907; abst. J.S.C.I. 1907, **26**, 537; U.S.P. 998995, 1911. E.P. 13983, 1904. D.R.P. 169930, 1904; abst. Mon. Sci. 1908, (4), **69**, 48. See also G. Kruger, Farb., Ztg. **18**, 289; abst. Jahr. Chem. 1905-08, II, 139; Chem. Ztg. 1908, **32**, 935; Chem. Tech. Rep. 1908, **32**, 544.

6. C. Stockhausen and Traiser, D.R.P. 246606, 1910; abst. C.A. 1912, **6**, 2541.

7. M. Bouffort, F.P. 16380, 16381, Add. of F.P. 443018; abst. Kunst. 1913, **3**, 116. C. Connor and J. Stubbs, E.P. 741, 1908; abst. J.S.C.I. 1909, **28**, 31; Chem. Tech. Rep. 1909, **33**, 515.

8. V. Boucheron, F.P. 366564, 1906; abst. J.S.C.I. 1906, **25**, 1056. See also M. Bouffort, F.P. 443018, 1912; abst. J.S.C.I. 1912, **31**, 1043.

9. C. Richardson and C. Forrest, J.S.C.I. 1905, **24**, 310; abst.

fats,[1] and rubber,[2] and as a generator of motive power.[3]

Dichlorethylene (Symmetrical 1.2-dichlorethylene, acetylene dichloride, CHCl:CHCl) may be prepared from tetrachlorethane either by treatment of the latter with iron, or aluminum and water;[4] or with iron, aluminum, zinc or water.[5] In the first method tetrachlorethane is suspended in water and submitted to the action of zinc dust. On the large scale the heat of reaction is so great as not only to render the use of external heat unnecessary, but in addition, to cause the continuous and regular distillation of pure dichlorethylene which boils at 55°. P. Askenasy and C. Vogelsohn[6] have devised a process for recovering zinc electrolytically from the zinc chloride obtained as a byproduct.[7] In the second method,

Jahr. Chem. 1905-08, II, 138.

1. O. Remmstedt, Chem. Ztg. 1909, **33**, 93; abst. J.S.C.I. 1909, **28**, 209.

2. For use in finishing bath for incandescent mantles, see Soc. du. Bec. Francais, F.P. 383705, 1907; abst. J.S.C.I. 1908, **27**, 397. For use in metal polish, see C. Ellis, U.S.P. 999491, 1911; abst. J.S.C.I. 1911, **30**, 1072. As a solvent in the manufacture of varnish, see L. E. Andes, Chem. Rev. Fett-u. Harz. Ind. 1905, **12**, 57; abst. J.S.C.I. 1905, **24**, 807.

3. A. Verley, F.P. 339134, 1903; abst. J.S.C.I. 1905, **24**, 78.

4. Konsortium fur Elektrochemische Industrie, D.R.P. 216070, 1907; abst. J.S.C.I. 1908, **27**, 37; Chem. Abst. 1910, **4**, 812; Zts. ang. Chem. 1910, **23**, 179; Chem. Zentr. 1910, II, 2103; Chem. Zts. 1910, **9**, 1538; Chem. Tech. Rep. 1909, **33**, 647; Mon. Sci. 1913, **78**, 159. F.P. 381430, 1907; abst. J.S.C.I. 1908, **27**, 92; Mon. Sci. 1909, **71**, ((4), 23), 101. Belg. P. 216918, 1909. D.R.P. 217554; abst. Mon. Sci. 1913, **78**, 160, is Add. to D.R.P. 216070. See Chem. Fabr. Griesheim-Elektron, D.R.P. 254069, 264006, 1913; abst. J.S.C.I. 1913, **32**, 212, 1029.

5. P. Askenasy and M. Mugdan, E.P. 19576, 1907; abst. J.S.C.I. 1908, **27**, 35; Chem. Tech. Rep. 1909, **33**, 32. U.S.P. 924304, 1909; abst. J.S.C.I. 1909, **28**, 746; Chem. Abst. 1909, **3**, 2200; Mon. Sci. 1910, **73**, 38.

6. Zts. Elektrochem, 1909, **15**, 773-79; abst. J.S.C.I. 1910, **29**, 45.

7. The apparatus used consisted of a wide-mouthed glass flask fitted with a cork stopper, through which was inserted a thermometer, a tube leading to the anode and a delivery tube. The anode consisted of a roll of platinum gauze enclosed in a cork-stoppered cylinder of porous earthenware, and suspended from a connecting wire, which passed through the anode tube. The latter fitted into the cork of the porous cylinder, holding the latter in position, and provided with a side tube connected with an upright condenser, and a chlorine-absorbing apparatus. The cathode consisted of a coil of copper wire wound around the diaphragm, the delivery tube being fitted with a reflux condenser surrounded by a fractionating apparatus. Tetrachlorethane was introduced into the flask with its

which is very similar to the first, the yield of dichlorethylene exceeds 90% of the theoretical calculated on tetrachlorinated ethane.

Commercial dichlorethylene has a specific gravity of 1.2902 at 15.6°, and is soluble in water less than 0.3% at the same temperature.[1] It is a heavy, colorless and nonhygroscopic liquid, of powerful narcotic but sweetish odor, uninflammable, non-combustible and non-explosive, an excellent solvent for caoutchouc, fats and some oils. Its low boiling point and ready volatility causes considerable losses in extraction and subsequent recovery, and calls for close attention to details when working with this solvent. It dissolves sandarac, elemi, mastic, dammar and the softer copals readily, shellac less easily and amber not at all. At least 85% by volume of commercial dichlorethylene should distil between the limits of 54-59°.[2] It is a nonsolvent of ether-alcohol soluble and insoluble cellulose nitrates, and of chloroform-soluble and acetone-soluble cellu-

surface some distance below the level of the bottom of the diaphragm and of the cathode. The flask being almost filled with an aqueous solution of zinc chloride, which was maintained very nearly, but not quite, at boiling temperature, while a silent electric current was passed through the apparatus. The delivery tube was filled with hot water kept at 65°, so that steam and tetrachlorethane vapor condensed while the lower boiling and more volatile dichlorethylene passed through the fractionating apparatus into an ice-cooled receiver. The authors conclude that using a 10% solution of zinc chloride, a cathode current density of 20 amperes per sq. dcm., a diaphragm surface of 3-4 sq. dcm. per kilo of dichlorethylene produced in 24 hours at a temperature of 97° an almost theoretical yield can be obtained, with a current efficiency of 80%, and an energy consumption of 3.7-4 kilowatt-hours per kilo of dichlorethylene.

1. Specific gravity mean of determination of seven samples from four separate sources. Solubility by the attempted solution of 3 cc. dichlorethylene in 1,000 cc. water at 15.6°, by 24 hours continuous shaking. C. Faust (Zts. physik. Chem. 1912, **79**, 99; abst. Chem. Zentr. 1913, I, 382; Bull. Soc. Chim. 1912, (4), **12**, 1092) gives the following density figures compared with water at 4°: 0°, 1.27; 10°, 1.252; 50°, 1.215. Timmermans (Sc. Proc. R. Dub. Soc. 1912, **13**, 326; Bull. Soc. Chim. Belg. 1912, **26**, 207; abst. Chem. Zentr. 1912, II, 1712) found sp. gr. 0°/4° equal to 1.28238.

2. The mean of the fractionation of seven liter samples with a four hours distillation for each, using a 4-bulb Ladenburg fractionating flask, gave the following results: 0-53.2 deg., 2 per cent.; 53.2-54 deg., 6 per cent.; 54-54.7 deg., 8 per cent.; 54.7-55.2 deg., 7.5 per cent.; 55.2-56.5 deg., 42 per cent.; 56.5-59.3 deg., 25 per cent; above 59.3 deg., 9 per cent. The first fraction was turbid, the second slightly, the other fractions clear.

lose acetates. In conjunction with alcohol and tetrachlorethane it imparts desirable properties in cellulose acetate mixtures. The Farbenfabriken vorm. F. Bayer have found [1] that dichlorethylene has no or only very low dissolving power for the cellulose esters which are suitable for the manufacture of lacquers and other flexible and plastic compounds, but in conjunction with alcohol, with or without the addition of other solvents such as acetone and chloroform, useful solutions are formed. Flexible films are said to result when a solution of 200 parts of cellulose acetate are mixed with 650 parts of dichlorethylene and 150 parts of alcohol, the solution allowed to settle, filtered and poured on plates.[2] Or, 120 parts of cellulose ester [3] are mixed with 730 parts of dichlorethylene and 150 parts of alcohol and slightly heated, the solution being employed for the uses above described. Or, 200 parts of cellulose ester [4] are thoroughly moistened with a mixture of 150 parts of ethyl alcohol, 400 parts of dichlorethylene and 250 parts of acetone. After allowing the mixture to stand for several hours it is in condition to be kneaded and pressed into forms, if necessary with warming.

1. E.P. 16932, 1910; abst. Mon. Sci. 1913, **78**, 86; J.S.C.I. 1910, **29**, 1299; Chem. Tech. Rep. 1911, **35**, 35. F.P. 418309, 1910; abst. J.S.C.I. 1911, **30**, 80. U.S.P. 988965, 1911; abst. J.S.C.I. 1911, **30**, 616; C.A. 1911, **5**, 2176; Mon. Sci. 1912, **77**, 30. Aust. Anm. 5592-10, July 11, 1910. The U. S. patent was taken out by T. Becker.

2. Prepared preferably according to D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahrsb. Chem. 1905-08, II, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, **60**, 54. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, **60**, 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. It. P. 62042, 1901. Aust. P. 31391.

3. Preferably prepared according to E.P. 24067, 1906; abst. J.S.C.I. 1907, **26**, 1213. F.P. 371447, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, **68**, 79; Chem. Tech. Rep. 1907, **31**, 149. For solvent action of dichlorethylene and epichlorhydrin upon cellulose and celluloid, see Flemming, J.C.S. 1896, i, 333; 1898, i, 396.

4. Preferably produced as in note above. For a method of preparing dichlorethylene by heating mixtures of acetylene and chlorine in capillary tubes to 150° or higher, see Chem. Fab. Griesheim Elektron, E.P. 16620, 1912; D.R.P. 254069, 1911; F.P. 446263, 1912; abst. Mon. Sci. 1913, **78**, 144; J.S.C.I. 1913, **32**, 312,

H. Dreyfus[1] produces new uninflammable celluloids by treatment of cellulose esters with neutral and indifferent bodies as anisol, phenetol, chloranisols, safrol, oil of camphor, benzyl alcohol and its chloro derivatives, *o*-dichlorbenzene, the chlortoluenes, the simple and chlorinated acetophenones, the benzophenones, and in general those bodies which possess neither acid nor free phenolic functions. These compounds are advantageously employed in conjunction with dichlorethylene and other chlorine-substituted methanes and ethanes, the process being particularly applicable to the cellulose acetates insoluble in chloroform, but soluble upon the addition of alcohol.

E. Fischer[2] has detailed the advantages of dichlorethylene as a solvent for crude caoutchouc, Siemens and Halske[3] having patented the same idea in France. Dichlorethoxyethylene[4] is still in the experimental stage as a solvent.

The specific gravity, boiling point and fractionation are sufficient indications of purity in the commercial product.

Trichlorethylene. $C_2H\,Cl_3$; may be prepared by the action of reducing agents as zinc and dilute sulfuric acid upon hexachlorethane;[5] by treatment of either tetrachlorethane with alcoholic potash;[6] from anhydrous chloral and phosphorus

213, 842; C.A. 1913, 7, 869; 1914, 8, 210. See also D.R.P. 264006, 1912; Add. to D.R.P. 254069; abst. C.A. 1914, 8, 211.

1. F.P. 432264, 1911; abst. J.S.C.I. 1912, 31, 24; Kunst. 1912, 2, 77. Belg. P. 241251, 1911. To emulsify dichlorethylene, see A. Schmidtz, D.R.P. 255901, 1908; abst. C.A. 1913, 7, 1989.

2. D.R.P. 211186, 1911; abst. C.A. 1909, 3, 2633; Zts. ang. Chem. 1909, 22, 1615; Chem. Zentr. 1909, II, 401; Chem. Tech. Rep. 1909, 33, 372. U.S.P. 910920, 1908; abst. Mon. Sci. 1910, 73, 135; C.A. 1909, 3, 1096. See D.R.P. 248984, 1910; abst. C.A. 1912, 6, 2981.

3. F.P. 386017, 1908; abst. J.S.C.I. 1908, 27, 759; C.A. 1909, 3, 1819; Mon. Sci. 1909, 71, 14.

4. G. Imbert, U.S.P. 894148, 1908; abst. J.S.C.I. 1908, 27, 876. F.P. 375167, 1907; abst. J.S.C.I. 1908, 26, 839. C. Netz & Co. (D.R.P. 267487, 1913; abst. J.S.C.I. 1914, 33, 72) employ dichlor- and trichlor-ethylene as a degreasing agent.

5. E. Fischer, Jenaisiche Zts. f. med. u. Naturw. I, 123; abst. Jahr. Chem. 1864, 481; Zts. Chem. Pharm. 1864, 268.

6. Berthelot and Jungfleisch, Compt. rend. 1869, 69, 542-546; abst. Instit. 1869, 289; Ber. 1869, 2, 560; Zts. Chem. 1869, 680; Jahr. Chem. 1869, 385; Bull. Soc. Chim. 1870, N.S. 13, 16-19. Ann. Suppl. 1870-1872, 7, 252-256.

pentasulfide at 160-170°;[1] or more recently,[2] by bringing acetylene tetrachloride into contact with a heated surface, some hexachlorbenzene being formed at the same time. The Chem. Fabrik Griesheim-Elecktron[3] vaporize acetylene tetrachloride at 110 to 760 mm. pressure, conduct over barium chloride previously heated to 300°, water being split off. After issuing from the reaction chamber, the vapors are conducted through a condenser, and then into cold water. The HCl is dissolved, while the trichlorethylene completely separates as an oily layer.

The Chemische Fabrik Buckau[4] prepare trichlorethylene by the action of thorium oxide upon tetrachlorethane at about 390°. When 200 gm. tetrachlorethane is passed through a glass rod heated to 360-390° in the presence of thorium nitrate, 68% of the theoretical amount of trichlorethylene is said to be obtained. Hexachlorbenzene in small amounts only is formed.

In order to obviate the formation of dichlorovinyl ether in

1. Paterno and Oglialoro, Gaz. Chim. Ital., 1873, **3**, 533; abst. Ber. 1874, **7**, 80; Bull. Soc. Chim. 1874, N.S. **22**, 73; Jahr. Chem. 1873, 464. In this connection see also H. Byasson, Compt. rend. 1872, **74**, 1290; Jahr. Chem. 1872, 442. E. Hagemann, Ber. 1872, **5**, 154; abst. Jahr. Chem. 1872, 443. For derivatives of trichlorethylene, see J. Boeseken, Rec. trav. Chim. 1913, **32**, 15; abst. C.A. 1913, **32**, 1702.

2. H. Tompkins and Clayton Aniline Co., E.P. 23780, 1906; abst. J.S.C.I. 1907, **26**, 778; C.A. 1907, **1**, 2520; Chem. Zts. 1907, **6**, 305; Chem. Tech. Rep. 1907, **31**, 360. In their preferred method the vapor of acetylene tetrachloride is passed through a tube in which the length is about 20 times the diameter and which contains a contact material such as pumice, heated to 400-500°. The vapor should be passed at such a rate that it has a faint brown color when discharged. The issuing vapor is condensed and washed with water in order to remove hydrochloric acid produced by the decomposition. Depending upon the rate of passage of the vapor, the products are trichlorethylene or hexachlorbenzene, together with a little unchanged acetylene tetrachloride. Trichlorethylene is produced at a lower and hexachlorbenzene at a higher temperature. According to the Chem. Fabr. Griesheim-Elektron (D.R.P. 263457, 1912; abst. J.S.C.I. 1913, **32**, 924; C.A. 1913, **7**, 4048), when acetylene tetrachloride is heated to about 300° with the chloride of a tetravalent metal, the products formed are pure trichlorethylene and hydrochloric acid only.

3. D.R.P. 263457, 1912; abst. C.A. 1913, **7**, 4048. F.P. 462-711, 1913; abst. J.S.C.I. 1914, **33**, 277.

4. D.R.P. 274782, 1912; abst. Kunst. 1914, **4**, 234; J.S.C.I. 1914, **33**, 807.

the usual process of preparing trichlorethylene by heating tetrachlorethane with alcoholic alkali solutions, The Konsortium fur Elektrochemische Industrie [1] replace the alcoholic solution by an aqueous solution or suspension of an alkaline solution, calcium hydroxide [2] having been found especially useful.

Trichlorethylene is a heavy, colorless, strongly refractive, non-hygroscopic liquid of soporific and narcotic chloroform-like odor, practically insoluble in water,[3] but miscible in all proportions without turbidity with methyl, ethyl or amyl alcohols, methyl, ethyl or amyl acetates, acetone, pyridine, nitrobenzene, benzine, benzene, toluene or xylene, and with chloroform and other chlorine substituted methanes, ethanes and ethylenes. The commercial product is usually sufficiently anhydrous to mix with paraffin oil without opalescence. The specific gravity of pure trichlorethylene is 1.4905 at 4°/4°, 1.4702 at 17.5°/17.5°, and 1.45987 at 25.5°/25.5°,[4] that of the

1. D.R.P. 171900, 1905; abst. J.S.C.I. 1907, **26**, 279; C.A. 1908, **2**, 571; Chem. Tech. Rep. 1906, **30**, 247; Chem. Zentr. 1906, II, 571; Zts. ang. Chem. 1907, **20**, 900; Mon. Sci. 1908, **69**, 39; Jahr. Chem. 1905-1908, II, 140.

2. D.R.P. 208834, 1907; being Add. to D.R.P. 171900, 1905; abst. C.A. 1909, **3**, 2210; Chem. Zentr. 1909, I, 1785; Chem. Tech. Rep. 1909, **33**, 248; Zts. ang. Chem. 1909, **22**, 986; Chem. Zts. 1909, **8**, 1440; Mon. Sci. 1913, **78**, 92.

3. That is, when 1 cc. trichlorethylene is shaken continuously for 48 hours with 500 cc. distilled water at 15.6° it is incompletely dissolved, from which it follows that the solubility in water is less than 0.2%.

4. H. Veley, Proc. Roy. Soc. 1910, **82**, 218-219; abst. J.S.C.I. 1910, **29**, 233; C.A. 1910, **4**, 1316; Chem. Zentr. 1910, I, 1275; Bull. Soc. Chim. 1911, (4), **10**, 170; J.C.S. 1910, **98**, i, 214. See also D. P. Ross. Van Lennep, Seifensieder Ztg. **40**, 369; abst. C.A. 1913, **7**, 2130. He found the boiling point of trichlorethylene to be 87.4-87.55° (corr.). Comparisons of the physiological actions with that of chloroform prepared from chloral hydrate showed that commercial trichlorethylene is rather more toxic than chloroform, while tetrachlorethane is four times more. Experiments with the pure compounds also showed that tetrachlorethane is four times, and trichlorethylene one and a half times more toxic than chloroform, molecule for molecule. In both cases the recovery from anaesthesia or paralysis is more regular than with chloroform. Of the several samples of commercial trichlorethylene fractionated by the writer, at least 85% came over between 86.7° and 88.9°. W. Herz and W. Rathman (Chem. Ztg. 1912, **36**, 1417; abst. Chem. Zentr. 1913, I, 229; J.C.S. 1913, **104**, i, 695; ii, 26; C.A. 1913, **7**, 1318, 3866), give the density of trichlorethylene as follows compared with water at 4 deg.: 17.6 deg., 1.466; 25 deg., 1.4542; 35 deg., 1.4376; 45 deg., 1.4211; 60 deg., 1.3964; 75 deg., 1.3722.

commercial product ranging from 1.47-1.482 at 15.6°/15.6°, in eight samples examined by the author. The boiling point is stated as 88°. The composite results of the fractionation of eight one liter samples in a 3-bulb Ladenburg distilling flask by the author, each being 4-hour distillations, gave the following results, the samples being from five separate sources: 0-58°, 2% turbid; 58-75°, 4%; 75-85°, 5%; 85-87°, 12%; 87-89°, 73%; above 89°, 4% (all by volume). Therefore a commercial trichlorethylene should give about 85% distillate between the ranges 85-89°. The residue upon evaporation to dryness of a 50 cc. quantity of each sample was less than 0.4%.

Trichlorethylene is a solvent of sulfur, phosphorus, fats, resins, mastic, sandarac, elemi and the softer copals. It is a non-solvent of ether-alcohol soluble and insoluble cellulose nitrates, and a non-solvent of not hydrated and acetone-soluble acetated cellulose. However, both alone and in combination with methyl and ethyl alcohols it has advantages in cellulose acetate mixtures, especially as an auxiliary solvent in conjunction with tetrachlorethane.

Chemische Fabrik Griesheim Elektron have found[1] that trichlorethylene suffers decomposition to the extent indicated by the following figures when heated for five days with an equal quantity of water in the presence of the following metals: Wrought iron, 0.04; cast iron, 0.04; copper, 0.03; lead, 0.015%.

1. Chem. Ztg. 1908, **32**, 256-257; abst. J.S.C.I. 1908, **27**, 344; Chem. Zentr. 1908, I, 1451; II, 292; Jahr. Chem. 1905-08, II, 139. L. Collardon (F.P. 453395, 1913; abst. J.S.C.I. 1913, **32**, 799), prepares cellulose ester paints and varnishes for the prevention of corrosion and fouling, in the following manner: Carbolic acid or other phenol or cresol is condensed with formaldehyde or paraformaldehyde in presence of one or more organic or inorganic compunds having toxic properties, e. g., copper sulphate or acetate, or compounds of lead, mercury, antimony, arsenic, zinc, etc. The product is mixed with one or more cellulose esters of the fatty series, e. g., formate, acetate, butyrate, palmitate, a solvent such as dichlorethylene, trichlorethylene, dichlorobenzene, acetone or carbon tetrachloride, and a pigment. Other substances such as jelutong or other rubber resins may be added to the phenol before condensing with the formaldehyde. In the case of the manufacture of a varnish, an oxidising bleaching agent is added with the formaldehyde; such agents are alkali peroxides, hydrogen peroxide, perborates, alkali percarbonates, persulphates or other alkali per-salts, hypochlorites, sulphur dioxide, either alone or in combination with borax or magnesia, hydrosulphites, or ozonised water.

Iron vessels, therefore, would appear to be suitable for use with this solvent.[1]

A. Zimmer[2] employed trichlorethylene in treating starched linen with cellulose acetate; while H. Dreyfus has described a series of noninflammable plastic masses[3] and celluloid substitutes,[4] in which that type of cellulose acetate which is insoluble or nearly so in tetrachlorethane alone but readily soluble upon the addition of alcohol, is treated with trichlorethylene and tetrachlorethane with or without mannol, camphor or other camphor substitute.

In the G. Koller process[5] acetylated cellulose derivatives, either alone or in combination with other cellulose esters, are

1. The small amount of iron dissolved, however, imparts to fats and oils a dark coloration, which cannot be removed by boiling with acids. Also on boiling trichlorethylene with alkalis or alkaline compounds in aqueous or alcoholic solution, hydrochloric acid is liberated, and gaseous products (probably dichloracetylene, and in presence of metals, monochloracetylene) are formed, which, in contact with air, may inflame or explode. Care must be taken when using trichlorethylene in open vessels, as it exerts a narcotic action several times stronger than carbon tetrachloride. Dichlorethylene and perchlorethylene are about as resistant to the action of metals as trichlorethylene. Perchlorethylene would probably be a useful solvent to employ in open vessels. Symmetrical tetrachlorethane and pentachlorethane are said to be much less resistant toward the action of metals. Trichlorethylene is physiologically less active than tetrachlorethane.

2. E.P. 12406, 1910; abst. J.S.C.I. 1911, **30**, 206. D.R.P. 242786, 1910; abst. C.A. 1912, **6**, 2182; Wagn. Jahr. 1912, II, 509. U.S.P. 1025731, 1912; abst. C.A. 1912, **6**, 1994. H. Koller (D.R.P. 266781, 1912) mixes cellulose esters with mono- or polyatomic phenols and tri- or per-chlorethylene, and thereby forms plastic celluloid-like masses of industrial value.

3. F.P. 432047, 1911; abst. J.S.C.I. 1912, **31**, 24; Belg. P. 241252, 1911.

4. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77; Belg. P. 241251, 1911.

5. E.P. 4744, 1911; abst. J.S.C.I. 1912, **31**, 328; C.A. 1912, **6**, 2315; F.P. 440133, 1912; abst. J.S.C.I. 1912, **31**, 680. D.R.P. 266781, 1912; abst. Kunst. 1914, **4**, 15; C.A. 1914, **8**, 573. U.S.P. 1079773, 1913. According to the patentee, when 1 part of an acetylized derivative of cellulose is mixed or ground with 2 parts of carbolic acid and then treated with 20 parts of perchlorethylene, a new gelatinous product results, forming a separate layer on top of the bulk of the perchlorethylene-phenol solution, from which it can be separated without difficulty. When the separated mass is freed from any excess of liquid absorbed by it, a semi-solid and plastic material remains, which can be pressed and shaped as desired, and which will, after the evaporation of the solvent, yield flexible products of a celluloid-like nature.

treated with trichlorethylene or perchlorethylene in the presence of mono- or poly-hydric phenols. On evaporation or removal of the solvent, a plastic material is obtained which is claimed to be a new compound, having special properties. The new compound may be obtained, for example, by taking one part of cellulose acetate, 2 of phenol and 20 parts of tri- or per-chlorethylene, and the finished compound obtained either by precipitation or evaporation. The solutions or plastic products are said to be especially suitable for covering or impregnating fibers, fabrics, etc., with a lustrous coating and for producing artificial filaments. Trichlorethylene is not a solvent of celluloid, and precipitates it from solutions. This precipitate may be brought into solution again by the addition of ethyl alcohol, due to the presence of camphor.

When heated with strong alkalis [1] it is gradually converted into dichloracetylene, but is stable toward weak alkalis (lime, sodium carbonate, soap) even in boiling solution. In analytical chemistry [2] it has been proposed as a solvent for fat as in milk analysis, and in the preparation of healing agents for tuberculosis [3] by the removal of fatty and waxy substances from tubercle bacilli by means of trichlorethylene.

Trichlorethylene is also of great interest as the starting point of a wide series of organic products which have hitherto been difficult to obtain technically, but which are or may be of considerable commercial importance. These reactions rest essentially on the greater reactivity of the chlorine atoms of trichlorethylene over the other ethylene chlorides.[4] Westrosol

1. According to Konsortium fur Elektrochemische Industrie, Chem. Ztg. 1908, **32**, 529-530; abst. J.S.C.I. 1908, **27**, 643; Zts. ang. Chem. 1908, **21**, 1805.

2. L. Gowing-Scopes, Anal., 1910, **35**, 238-244; abst. J.S.C.I. 1910, **29**, 844; C.A. 1910, **4**, 2783; Merck's Rep. 1910, **19**, 323; Drug. Circ. 1910, **54**, 571; J.C.S. Soc. 1910, **98**, ii, 647; Chem. Zentr. 1910, II, 412; Zts. ang Chem. 1911, **24**, 899; Chem. Tech. Rep. 1910, **34**, 409.

3. Chem. Fab. auf Actien (vorm. E. Schering), D.R.P. 248984, 1910; abst. C.A. 1912, **6**, 2981. For the determination of fat in leather by means of trichlorethylene, see E. Goldberg, Ledertech. Rundsch, 1912, **4**, 49; abst. J.S.C.I. 1912, **31**, 596; C.A. 1913, **7**, 1634.

4. For instance, under the action of caustic soda, lime and alcohol, trichlorethylene exchanges one of its chlorine atoms with the

and Tri are commercial names for this solvent. B. Szanyi [1] has patented the use of trichlorethylene in conjunction with carbon tetrachloride and pentachlorethane as a non-combustible and non-explosive solvent for dried oil color and lac coatings.

Perchlorethylene (Tetrachlorethylene) may be formed by the action of strong heat upon hexachlorethane,[2] by long boil-

ethoxy group and is converted smoothly into dichlorvinyl ether (Imbert and Konsortium fur Elektrochemische Industrie, D.R.P. 216940; abst. Chem. Tech. Rep. 1910, 84, 45; Chem. Zentr. 1910, I, 308; Zts. ang Chem. 1910, 23, 179; Chem. Zts. 1910, 9, 1674), the reaction being $C_2HCl_3 + C_2H_5ONa = C_2HCl_2OC_2H_5 + NaCl$. Dichlorvinylether is a compound of extraordinary reactive power, which also adds HCl as smoothly as chlorine, with solution of the double compound. The chlorine addition product thus obtained splits up on distillation into ethyl chloride and is converted into chloracetylchloride or dichloracetylchloride according to the equations:

$$C_2H_2Cl_3OC_2H_5 = C_2H_2Cl_2O + ClC_2H_5;$$
$$C_2HCl_4OC_2H_5 = C_2HCl_3O + ClC_2H_5.$$

According to these reactions the two chlorinated acetyl chlorides are obtained, which themselves contain very reactive chlorine atoms, and therefore are applicable to many syntheses. More important than this reaction of dichlorvinylether is its conversion with water into chloracetic ester (Imbert and Konsortium fur Elektrochemische Industrie, D.R.P. 209268; abst. Chem. Tech. Rep. 1909, 33, 289; D.R.P. 210502; abst. Chem. Tech. Rep. 1909, 33, 362; D.R.P. 216716; abst. Chem. Tech. Rep. 1910, 33, 32), the reaction being $C_2HCl_2OC_2H_5 + H_2O = C_2H_2ClOOC_2H_5 + HCl$. This reaction takes place quantitatively under the catalytic action of a trace of HCl at ordinary temperatures. As labile intermediate substance there is formed the above mentioned hydrogen chloride addition compound. In this way the chloracetic ester, which hitherto has been obtained only as a conversion compound of acetic acid, is technically prepared from acetylene, chloracetic ester being an old and much used starting point for synthetic work. In decomposing, it is able on the one hand to retain the chlorine and split off the alcohol, while under other conditions it exchanges its chlorine, retaining its ester characteristics. Furthermore, in almost all cases the exchange of both groups is practicable. Thus chloracetamide is formed from chloracetic ester under the action of ammonia, according to—$C_2H_2ClCOOC_2H_5 + NH_3 = C_2H_2ClCONH_2 + C_2H_5O$. The ester is converted into aniline (1 mol.) in the presence of calcium carbonate into phenylglycin ester (D.R.P. 194884; abst. Chem. Tech. Rep. 1908, 32, 123), the latter with an alkaline carbonate going into phenylglycin salt. In this manner the way from acetylene to indigo is made clear, another importance of the method lying in the fact that acetylene is only half the price of acetic acid.

1. D.R.P. 234264, 1910; abst. J.S.C.I. 1911, 30, 815; C.A. 1911, 5, 2982; Kunst. 1912, 2, 100; Chem. Zentr. 1911, I, 1662; Zts. ang. Chem. 1911, 24, 1102; Chem. Tech. Rep. 1910, 34, 324. D.R.P. 273344, 1913, being Add. to D.R.P. 234264; abst. Kunst. 1914, 4, 235, includes paraffin and halogenized benzene and phenols for the formation of plastic masses with acetylcellulose.

2. Faraday Ann. Chim. Phys. 1821, (2), 18, 48; Phil. Trans.

ing of chloral with aluminum chloride,[1] by distilling hexachlorethane with aniline,[2] or with zinc and dilute sulfuric acid.[3] Perchlorethylene is a colorless, refractive liquid of heavy narcotic odor, sp. gr. 1.62 at 19°, and boiling at 121°.[4]

Perchlorethylene has been patented by G. Koller[5] as a cellulose acetate solvent in conjunction with phenol.

Chlorhydrins, as mono-, di-and epi-chlorhydrin, and especially their derivatives, have been found valuable solvents and plastic-inducing bodies in combination with the various acetylated celluloses. Monochlorhydrin is used primarily in the explosives industry.[6] The dichlorhydrins, i. e., *a*-dichlorhydrin, sp. gr. 1.367 at 19°, b. pt. 174°, and *b*-dichlorhydrin, sp. gr. 1.379° and boiling at 182.3°, may readily be prepared by treating glycerol with excess of hydrochloric acid,[7] or sulfur chloride,[8] by shaking epichlorhydrin with fuming hydrochloric

1821, 47.

1. A. Combes. Ann. Chim. Phys. 1887, (6), **12**, 269; Bull. Soc. Chim. 1887, (2), **48**, 465.

2. E. Bourgoin, Bull. Soc. Chim. 1875, (2), **23**, 344; Chem. Centr. 1875, 421; Compt. rend. **80**, 971; Ann. Chim. Phys. (5), **6**, 142.

3. A. Geuther, Ann. 1858, **107**, 212.

4. R. Schiff, Ann. 1883, **220**, 97; Chem. Centr. 1883, 749; Jahr. Chem. 1883, 63; J.C.S. 1883, **44**, 1044; Bull. Soc. Chim. 1883, **40**, II, 444.

5. E.P. 4744, 1911; abst. J.S.C.I. 1912, **31**, 328; C.A. 1912, **6**, 2315. F.P. 440133, 1912; abst. J.S.C.I. 1912, **31**, 680; Kunst. 1912, **2**, 355, 439.

6. See E. I. du Pont de Nemours Powder Co., U.S.P. 1040323, 1912; abst. Mon. Sci. 1913, **78**, 13; J.S.C.I. 1912, **31**, 1054. D.R.P. 229536, 1910; abst. J.S.C.I. 1911, **30**, 307. Chem. Fabrik Griesheim-Elektron, D.R.P. 238341, 1908; abst. C.A. 1912, **6**, 1660. Deutsche Sprengstoff Aktiengesellschaft, E.P. 26036, 1911; abst. J.S.C.I. 1912, **31**, 1147; C.A. 1913, **7**, 807. F.P. 370224, 370249, 1906; abst. Mon. Sci. 1908, (4), **68**, 78. F.P. 437315, 1911; abst. J.S.C.I. 1912, **31**, 557; C.A. 1912, **6**, 2674. D.R.P. 254709, 1912; abst. C.A. 1913, **7**, 807. Belg. P. 194975, 1906. Chem. Fabr. von Heyden, D.R.P. 263106, 1912; abst. C.A. 1913, **7**, 3820; J.S.C.I. 1913, **32**, 925. P. Walden and R. Swinne (Zts. Physik. Chem. 1912, **79**, 713; abst. Chem. Zentr. 1912, II, 791; Bull. Soc. Chim. 1912, (4), **12**, 1250; C.A. 1912, **6**, 2877; J.C.S. 1912, **102**, ii, 628) give the density of monochlorhydrin as follows: 25°/4°, 1.3181; 50°/4°, 1.2594; 70°, 1.2773.

7. A. Berthelot, Ann. 1854, **92**, 302; Compt. Rend. 1854, **38**, 668; Instit. 1854, 116; Jour. Pharm. 1854, (3), **25**, 346; Ann. ph. nat., **26**, 81; J. pr. Chem. 1854, **62**, 133; Pharm. Centr. 1854, 401; Jahr. Chem. 1853, 455.

8. L. Carius, Ann. 1862, **122**, 73; **124**, 221; Chem. Centr. 1862, 588; Jahr. Chem. 1862, 452; Zeit. Chem. Pharm. 1862, 711. Chem.

acid,[1] or by passing HCl gas at 120-130° through glycerol.[2] The chlorhydrins (dichlorisopropyl alcohols) are direct solvents of acetone-soluble acetylcellulose.[3] C. Weber and C. Cross prepare cellulose butyrate in the presence of dichlorhydrin.[4] The action of acetation may be modified by its presence as a diluent,[5] the cellulose acetate being either so esterified

Centr. 1862, 993; Ann. Chim. Phys. (3), **66**, 202; Rep. Chim. Pure. 1862, (4), 227, 429; **5**, 364. A. Claus, Ann. 1873, **168**, 42; Chem. Centr. 1873, 688.

1. E. Reboul, Ann. suppl. 1861, **1**, 225; Ann. Chim. Phys. 1860, (3), **60**, 5; Bull. Soc. Chim. 1860, **2**, 411. See J. Niviere (Bull. Soc. Chim. 1913, (4), **13**, 969; abst. J.C.S. 1913, **104**, i, 697, 1299) for preparation of epichlorhydrin.

2. A. Fauconnier and J. Sanson, Bull Soc. Chim. 1887, (2), **48**, 237; Chem. Centr. 1887, 1194; Jahr. Chem. 1887, 1252. Bull. Soc. Chim. 1886, (2), **50**, 212; Chem. Centr. 1888, 1349; Jahr. Chem. 1888, 1407; J.C.S. 1888, **54**, 244. A. Bigot, Ann. Chim. Phys. 1891, (6), **22**, 437; Chem. Centr. 1891, 863; Jahr. Chem. 1891, 1333. A. Watt, Ber. 1872, **5**, 258; Jahr. Chem. 1872, 327. See also Hubner and Muller, Jahr. Chem. 1870, 472; Chem. Centr. 1870, 659.

3. E.P. 24067, 1906; abst. J.S.C.I. 1907, **26**, 1213. F.P. 371-447, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 22, 79; Chem. Tech. Rep. 1907, **31**, 149. U.S.P. 1015155, 1912; Mon. Sci. 1912, **77**, 163. Swiss P. 52437; abst. Kunst. 1912, **2**, 135. Aust. P. 47889. U.S.P. 1015156, 1912; Mon. Sci. 1912, **77**, 163. E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1005; Chem. Tech. Rep. 1911, **35**, 340. E.P. 18076, 1910, being First Add. to E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1199. F.P. 412797, 1910; abst. J.S.C.I. 1910, **29**, 1005; Rev. Chim. Ind. 1910, **21**, 257. First Add. 12388, dated Mar. 19, 1910, to F.P. 412797, 1910; abst. J.S.C.I. 1910, **29**, 1199. D.R.P. 238348, 1909; abst. C.A. 1912, **6**, 1672; Chem. Zentr. 1911, **82**, 1085; Chem. Ind. 1911, **34**, 637; Chem. Tech. Rep. 1911, **35**, 520. Aust. P. 47899. Swiss. P. 52115; abst. Kunst. 1912, **2**, 99. Can. P. 129265, 1910. E.P. 27258, 1910; abst. J.S.C.I. 1911, **30**, 1112; C.A. 1912, **6**, 1526. Can. P. 129983, 1910. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770; C.A. 1912, **6**, 2687. E.P. 11354, 1909; abst. J.S.C.I. 1910, **29**, 752. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. F.P. 408370, 1910; abst. J.S.C.I. 1910. **29**, 624. First Add. No. 12469, dated April 13, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1299. Second Add. dated June 11, 1910, to F.P. 408370; abst. J.S.C.I. 1910, **29**, 1371. Aust. P. 29b, 4642-10, June 21, 1909.

4. U.S.P. 632605, 1899. E.P. 22029, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 63101, 1899. D.R.P. 112817. Russ. P. 3264, 1900. Belg. P. 137577, 1898. Dan. P. 2558, 1899. Port. P. 2930, 1899.

5. U.S.P. 627031, 1899. E.P. 18283, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 62188, 1899. F.P. 282320, 1899. Russ. P. 3378, 1900. Dan. P. 2636, 1899. Luxom. P. 3302, 3361, 7610, 1898. Port. P. 2899, 1899. Belg. P. 138462, 1898. Add. to Belg. P. 137577. Norw. P. 7610, 1898. Hung. P. of Aug. 31, 1898, and Nov. 8, 1898.

as to combine with the dichlorhydrin,[1] or be but partially soluble in it.[2]

A series of patents have been granted to W. Lindsay for ethylenechlorhydrin,[3] ethyleneacetochlorhydrin,[4] ethylene chloride and alcohol,[5] and acetodichlorhydrin and alcohol,[6] as cellulose acetate solvents, and ethylenechlorhydrin [7] and ethyleneacetochlorhydrin [8] as nitrocellulose solvents. Ethylenechlorhydrin, a compound boiling at 129°, has a strong solvent power for acetylcellulose, solutions made therefrom having a high viscosity and volatilizing slowly. This solvent is miscible and may be used in conjunction with alcohol, ether, acetone, chloroform or tetrachlorethane. Ethyleneacetochlorhydrin boils at about 145,° is practically insoluble in water, and is especially applicable as a solvent for those forms of acetylcellulose which dissolve in substantially anhydrous acetone, or are plastic in warm chloroform. Lindsay has found in producing a compound solvent with ethylene chloride and methyl alcohol, that if either constituent be increased over the ratio of 1 to 2.5, the solvent action decreases, whereas an excellent solvent results when ethylenechloride and ethyl alcohol are mixed in equal proportions. The solvent action of acetodichlorhydrin is materially increased by the addition of either methyl or ethyl alcohol, three parts of chlorhydrin to two of alcohol being especially efficient.

Epichlorhydrin (chlorbutylenehydroxide) has long been known as an efficient solvent of nitrocellulose, and was patented for that purpose by Flemming [9] and by E. Mueller.[10] It

1. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264, 1911; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

2. F.P. 385179, 385180, 1907; abst. J.S.C.I. 1908, **27**, 589; C.A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 105, 106; Bull. Soc. Chim. 1909, (4), **6**, 567.

3. U.S.P. 1027614, 1912; abst. J.S.C.I. 1912, **31**, 583; Mon. Sci. 1912, **77**, 163.

4. U.S.P. 1027615, 1912; abst. J.S.C.I. 1912, **31**, 583.

5. U.S.P. 1027616, 1912; abst. J.S.C.I. 1912, **31**, 583; Mon. Sci. 1912, **77**, 163.

6. U.S.P. 1027486, 1912; abst. J.S.C.I. 1912, **31**, 583; Mon. Sci. 1912, **77**, 164.

7. U.S.P. 1027617, 1912; abst. J.S.C.I. 1912, **31**, 584.

8. U.S.P. 1027618, 1912; abst. J.S.C.I. 1912, **31**, 584.

may be prepared by heating glycerol with phosphorus pentachloride;[1] or by treating dichlorhydrin either with dilute alkaline saponifying agents[2] or an alkaline or alkaline-earth carbonate at a temperature preferably under 100°.[3] Epichlorhydrin is a colorless liquid boiling at 117°, sp. gr. 120, practically insoluble in water, but miscible in all proportions with alcohol, ether, amyl or ethyl acetates, acetone or acetylene tetrachloride. It is an especially energetic solvent for those acetylcelluloses which also dissolve in acetone. For modifying the process of acetation[4] in the preparation of both cellulose acetate and butyrate,[5] it is inferior to non-solvents as benzene and carbon tetrachloride. Plastics of acetylcellulose and epichlorhydrin may readily be prepared[6] by the aid of

9. Must. Z. 1897, **46**, 313.

10. D.R.P. 222777, 1909.

1. A. Berthelot, Ann. Chim. Phys. 1854, (3), **41**, 229. See also A. Claus and Nahmacher, Ber. 1872, **4**, 356; Jahr. Chem. 1872, 622; Chem. Centr. 1872, 467; and A. Lourenco, Compt. rend. **52**, 1043; Zts. Chem. Pharm. 1861, 364. Phil. Mag. 1861, (4), **22**, 135; Jour. pr. Chem. 1862, **85**, 502; Rev. Chim. Pure. **8**, 337. Ann. 1861, **120**, 89; Jahr. Chem. 1861, 654; 1867, 574.

2. D.R.P. 239077, 1910; abst. J.S.C.I. 1911, **30**, 1409; Chem. Zentr. 1911, **82**, [(5), **15**], II, 1393; Zts. ang. Chem. 1911, **24**, 2132; Chem. Tech. Rep. 1911, **35**, 596; C.A. 1911, **5**, 1393. J. Niviere (Bull. Soc. Chim. **13**, 969; abst. C.A. 1913, **7**, 3113; 1914, **8**, 657) prepares epichlorhydrin by reacting under 120 mm. pressure of 2 molecules of dichlorpropyl alcohol with 2 molecules of lime, calcium chloride, calcium hydroxide and epichlorhydrin being formed, the latter giving a yield at 93-95% of the theoretical.

3. E.P. 24067, 1906; abst. J.S.C.I. 1907, **26**, 1213. F.P. 371447, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, (4), **68**, 79; Chem. Tech. Rep. 1907, **31**, 149. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, (4), **60**, 17. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, (4), **60**, 54. Aust. P. 31391. It. P. 62042, 1901. D.R.P. 246242, 1910; abst. C.A. 1912, **6**, 2496; J.S.C.I. 1912, **31**, 605; Chem. Zentr. 1912, **82**, I, 1677.

4. U.S.P. 627031, 1899. E.P. 18283, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 62188, 1899. F.P. 282320, 1899. Russ. P. 3378, 1900. Dan. P. 2636, 1899. Luxem. P. 3302, 3361, 7610, 1898. Port. P. 2899, 1899. Belg. P. 138462, 1898; Add. to Belg. 137577. Norw. P. 7610, 1898. Hung. P. Aug. 31, 1898; Nov. 8, 1898.

5. U.S.P. 632605, 1899. E.P. 22029, 1898; abst. J.S.C.I. 1899, **18**, 756. Can. P. 63101, 1899. D.R.P. 112817. Russ. P. 3264, 1900. Belg. P. 137577, 1898. Dan. P. 2558, 1899. Port. P. 2930, 1899.

alcohol or acetone, assisted by a low degree of heat. Maas & Waldstein Co.[1] prepare chlorhydrin cellulose ester solvents by mixing a fixed alkaline bicarbonate with an alkaline hypochlorite and an olefine. W. Lindsay[2] dissolves acetylcellulose in trichlorhydrin mixed with an equal volume of methyl or ethyl alcohol, or in a mixture of pentachlorethane and methyl alcohol in the same relative proportions.

Tetrachlorethane[3] (Sym.-1. 1. 2. 2.—tetrachlorethane, Acetylene tetrachloride, Vitrol, Vitran, Westron) may be prepared from acetylene and antimony pentachloride;[4] from dichloraldehyde and phosphorus pentachloride;[5] by heating

6. U.S.P. 1015156, 1912; abst. Mon. Sci. 1912, **77**, 163. E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1005; Chem. Tech. Rep. 1911, **35**, 340. E.P. 18076, 1910; being First Add. to E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1199. F.P. 412797, 1910; abst. J.S.C.I. 1910, **29**, 1005; Mon. Sci. 1913, **78**, 76; Rev. Chim. Ind. 1910, **21**, 257. First Add. 12388, Mar. 19, 1910, to F.P. 412797, 1910; abst. J.S.C.I. 1910, **29**, 1199. D.R.P. 238348, 1909; abst. C.A. 1912, **6**, 1672; Chem. Zentr. 1911, **82**, 1085; Chem. Ind. 1911, **34**, 637; Chem. Tech. Rep. 1911, **35**, 520. Aust. P. 47899. Swiss P. 52115; abst. Kunst. 1912, **2**, 99. Can. P. 129265, 1910. D.R.P. 200334, 1907; abst. J.S.C.I. 1908, **27**, 1130; Mon. Sci. 1911, (5), **74**, 63; Chem. Zts. 1908, **7**, 909; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, 655: Jahr. Chem. 1905-08, II, 987; J.C.S. 1908, **94**, i, 955; Chem. Ind. 1908, **31**, 499.

1. Can. P. 132232, 1911.

2. U.S.P. 1041114, 1912; abst. J.S.C.I. 1912, **31**, 1075; C.A. 1912, **6**, 3517; Mon. Sci. 1913, **79**, 110.

3. For resume of technical applications of tetrachlorethane, containing 33 patent and 98 literature references, see E. C. Worden and L. Rutstein, Kunst. 1913, **3**, 83; abst. C.A. 1913, **32**, 4049. See also F. Frankfort, Chem. Ztg. 1908, **32**, 256; abst. Bull. Soc. Chim. 1909, (4), **6**, 229. W. Herz and W. Rathmann, Chem. Ztg. 1912, **36**, 1417; abst. J.S.C.I. 1913, **32**, 46.

4. Berthelot and Jungfleisch, Compt. rend. 1869, **69**, 542; abst. Instit. 1869, 289; Ber. 1869, **2**, 560; Zts. Chem. 1869, 680; Jahr. Chem. 1869, 385; Bull. Soc. Chim. 1870, **13**, 16; Ann. Suppl. 1870-72, **7**, 252-256. They found that acetylene unites with antimony pentachloride to a double compound $SbCl_5C_2H_2$, which is decomposed when heated with antimony pentachloride at strongly elevated temperatures, into acetylene tetrachloride and antimony trichloride. The reaction was performed in a distilling apparatus so that the acetylene tetrachloride contaminated with antimony pentachloride was condensed in a receiver. When this double compound of acetylene tetrachloride and antimony pentachloride was heated alone, symmetrical dichlorethylene (acetylene dichloride) distilled off. All endeavors to unite acetylene and chlorine directly were unsuccessful on account of frequent violent explosions. Romer (Ann. 1886, **233**, 183) claims perfectly pure acetylene combines calmly with chlorine in the light.

5. Paterno and Pisati, Jahr. Chem. 1871, 508.

ethylene chloride with the calculated quantity of phosphorus pentachloride for ten hours at 190°[1] and by passing acetylene into phosphorus pentachloride, explosion often occurring,[2] and by heating ethylene chloride to 110° with aluminum chloride.[3]

In the later process of P. Askenasy and M. Mugden[4] acetylene is fed into antimony pentrachloride, the latter being preferably free from chlorine and diluted with a suitable medium as acetylene tetrachloride. Chlorine is then added and finally more acetylene, the product being a mixture of antimony pentachloride, acetylene tetrachloride and small quantities of products of substitution of the latter body. T. H. Tompkins claims[5] the explosive tendency of the reaction between acetylene and antimony pentachloride is due to the presence of excess of chlorine in the latter, and can be prevented by insuring the presence of a certain proportion of antimony trichloride during the passage of the acetylene.[6] F.

1. A. Colson and H. Gautier, Compt. rend. 1886, **102**, 1076; abst. Jahr. Chem. 1886, 628; J.C.S. 1886, **50**, 231. See also Colson and Gautier, Compt. rend. 1885, **101**, 1064; abst. Chem. Centr. 1886, **57**, 20. Bull. Soc. Chim. 1886, **45**, 6; abst. Chem. Centr. 1886, **57**, 85. Ann. Chim. Phys. 1887, (6), **11**, 19; abst. Chem. Centr. 1887, **58**, 690.

2. Sabanejeff, Ann. 1883, **216**, 262.

3. Mouneyrat, Bull. Soc. Chim. 1898, (3), **19**, 447-452; abst. J.C.S. 1899, **76**, i, 241. He heated ethylene chloride to which had been added aluminum chloride to a temperature of 70-75°, and introduced chlorine and acetylene into the liquid. The gases combined when all air was excluded, acetylene tetrachloride being formed, in conjunction with some hexachlorethane. See Mon. Sci. 1906, **64**, 113. Belg. P. 250816; abst. C.A. 1913, **7**, 235.

4. U.S.P. 804516, 1906; abst. Mon. Sci. 1906, **64**, 68; Chem. Zts. 1906, **5**, 18; E.P. 18602, 1904; abst. Mon. Sci. 1906, **65**, 179; J.S.C.I. 1905, **24**, 150. Of the many decompositions of tetrachlorethane, there are two quantitatively occurring reactions which have become technically important and which are described in detail elsewhere in this work. On the one hand with base metals in the presence of water and heat, dichlorethylene is formed with the splitting off of two atoms of chlorine, while with lime it is converted into trichlorethylene. For general articles on tetrachlorethane, see Chem. Fabrik Griesheim Elektron, Chem. Ztg. 1908, **32**, 256-7; abst. Jahr. Chem. 1905-08, II, 139. Konsortium f. Elektrochem. Industrie, Chem. Ztg. 1907, **31**, 1095-96; 1908, **32**, 528; abst. Bull. Soc. Chim. 1909, (4), **6**, 230.

5. E.P. 19568, 1904; abst. J.S.C.I. 1905, **24**, 902; Mon. Sci. 1906, **65**, 179. D.R.P. 196324, Jahr. Chem. 1905-08, II, 139. See also F. Sparre and W. Masland, Can. P. 147424, 1913; abst. C.A. 1913, **7**, 2096.

Michel [1] leads chlorine gas into a mixture of sulfur chloride

6. The best yields were found to be obtained by adjusting the quantity of acetylene so that the liquor at the end of the absorption has the composition $SbCl_5.C_2H_2 + SbCl_5 + xSbCl_5$. When this liquor is distilled in small quantities at a time the production of acetylene tetrachloride is almost quantitative. If one-third of the total antimony be present in the form of the trichloride, the mixture may be heated to a temperature of 120° during the passage of the acetylene, in which case the acetylene tetrachloride is produced directly. Acetylene dichloride is produced together with the tetrachloride when the saturation with the acetylene is carried to the point of completion. Trichlorethylene is prepared by the action of alcoholic ammonia upon acetylene tetrachloride.

1. Zts. ang. Chem. 1906, **19**, 1095-97; abst. Chem. Centr. 1906, II, 746; Jahr. Chem. 1905-08, II, 140; J.S.C.I. 1906, **25**, 713. When absorption slackens, excess of acetylene is expelled by carbon dioxide, and chlorine led in. The alternation of chlorine and acetylene is kept up until neither gas is absorbed to any appreciable extent. The mixture is then shaken with water to decompose the remaining sulfur chloride present, and steam distilled. The distillate is washed with dilute sodium carbonate solution, separated from this, dried, and fractionated. Although chiefly s-tetrachlorethane, there is always small amounts of penta- and hexa-compounds present. In the process of the Konsortium f. Elektrochemische Industrie (D.R.P. 154657, 1903. F.P. 346562, 1904; abst. J.S.C.I. 1905, **24**, 209. E.P. 18602, 1904; abst. J.S.C.I. 1905, **24**, 150; Chem. Zts. 1905, **4**, 64; Mon. Sci. 1906, **65**, 12), acetylene and chlorine are introduced into antimony pentachloride alternately or simultaneously, but in different portions of the reacting apparatus, so that the gases do not come in contact with each other. In this manner a gradual combination of both gases to acetylene tetrachloride takes place, a good yield being obtained. By introducing the acetylene into antimony pentachloride the double compound $SbCl_5C_2H_2$ is first formed, together with the double compound $SbCl_5 2C_2H_2$, and these react with more chlorine to produce tetrachlorethane, with the reformation of antimony pentachloride. The antimony salt then reacts again with acetylene, and this process continues without visible loss of antimony salt. Out of the general reaction product the acetylene tetrachloride may be separated by fractional distillation, because during the distillation the antimony pentachloride (b. pt. 157°) is transformed into the trichloride which boils at 213°, hence the acetylene tetrachloride can be distilled away from the antimony. During this distillation, however, the chlorides of antimony chlorinate small amounts of tetrachlorethane into penta- and hexa-chlorethane, while the acetylene tetrachloride is distilling off. The trichloride of antimony is charged into the pentachloride and re-used. According to the Salzbergwerk Neu Stassfurt (F.P. 355776, 1905; abst. J.S.C.I. 1905, **24**, 1255; Mon. Sci. 1907, **67**, 38. D.R.P. 174068, 1904; abst. Chem. Tech. Rep. 1906, **30**, 313; Jahr. Chem. 1905-08, II, 140. D.R.P. 185347, 1905; abst. Jahr. Chem. 1905-08, II, 139; Chem. Zentr. 1907, II, 499; Zts. ang. Chem. 1907, **20**, 2046; Chem. Tech. Rep. 1907, **31**, 319. E.P. 1105, 1912; U.S.P. 1036224, 1912; abst. J.S.C.I. 1912, **31**, 458, 901), acetylene can be safely chlorinated by allowing it to act on a mixture of sulfur chloride and a catalyser such as iron and ferric compounds. To produce tetrachlorethane it is best to saturate the mixture of sulfur chloride and the catalyser with acetylene,

with 1% of its weight of reduced iron, the unabsorbed chlorine expelled by carbon dioxide, and dry acetylene led in, the temperature meanwhile being kept below 40°. In order to obviate the explosive reaction with which acetylene and chlorine combines in sunlight, J. Lidholm [1] modifies and controls the reactive force by diluting the gases with an indifferent gas as carbon dioxide and afterwards exposing the gas mixture to the action of chemically active or actinic rays, whereby the reaction proceeds very calmly. Radium rays, Roentgen rays, and ultraviolet light are cited as examples, especially suitable being the ultraviolet rays which are emitted from quartz mercury lamps. In another process [2] explosion is minimized by introducing the acetylene and chlorine through separate tubulures into a reaction tube containing coarse gravel in its lower portion, a mixture of fine sand and iron filings in its middle portion, and pure sand on top, the whole being surrounded by a cooling jacket. The process of J. Voigt [3] is similar. G. Orn-

cooling if necessary, the tetrachlorethane then being obtained by fractionation. If the mixture after being saturated with acetylene, is saturated with chlorine at the boiling temperaure, hexachlorethane separates on cooling. See also F.P. 433309, 1911; U.S.P. 1045189, 1912; abst. J.S.C.I. 1912, **31**, 153; 1913, **32**, 47; Zts. ang. Chem. 1906, **19**, 1095-1097; abst. J.S.C.I. 1906, **25**, 713. Compare Konsortium f. Elektrochemische Industrie, Ges. E.P. 25967, 1910.

1. D.R.P. 201705, 1905; abst. Jahr. Chem. 1905-08, II, 140; C.A. 1909, **3**, 359; Chem. Zentr. 1908, II, 1071; Zts. ang. Chem. 1908, **21**, 2234; Chem. Zts. 1909, **8**, 1045. Norw. P. 16873, 1905; abst. Chem. Tech. Rep. 1907, **31**, 634. U.S.P. 831725, 1906; abst. J.S.C.I. 1906, **25**, 1067; Mon. Sci. 1907, **67**, 551; C.A. 1909, **3**, 359. F.P. 358146, 1905; abst. C.A. 1907, **1**, 666; J.S.C.I. 1906, **25**, 197; Chem. Zts. 1906, **5**, 38. E.P. 22094, 1905; abst. J.S.C.I. 1906, **25**, 713; Chem. Zts. 1903-04, **3**, 117. French patent taken out by Alby Carbidfabr. Aktiebolag.

2. Chemische Fabrik Griesheim Elektron, F.P. 378713, 1907; bst. J.S.C.I. 1907, **26**, 1215; Mon. Sci. 1909, **71**, 97; C.A. 1909, **3**, 2208. E.P. 13411, 1907; abst. Chem. Ztg. 1909, **33**, 32; J.S.C.I. 1908, **27**, 296. D.R.P. 204883; abst. C.A. 1909, **3**, 1457. D.R.P. 204883; abst. Chem. Zentr. 1909, I, 325; Chem. Zts. 1909, **8**, 1115; Chem. Tech. Rep. 1909, **33**, 23; Zts. ang. Chem. 1909, **22**, 214. Belg. P. 200926, 1907. According to another variation of their process, the whole tube is filled with sand, the lower portion being immersed in an absorbing liquid as antimony pentachloride in which the reaction takes place.

3. U.S.P. 908051, 1908; abst. C.A. 1909, **3**, 947; J.S.C.I. 1909, **28**, 109. F.P. 378713, 1907; abst. J.S.C.I. 1907, **26**, 1215. See H. Brandenburg, Belg. P. 205575, 1908.

stein[1] claims to obviate the disadvantages of the foregoing described processes by causing acetylene to act upon chlorine dissolved in acetylene tetrachloride and in the presence of such means as are capable of accelerating chemical action, for instance a non-volatile catalyzing agent as iron, in the shape of filings or shavings. The presence of a foreign body as a diluting agent is not required.[2] Ferric chloride has also been patented as the catalytic agent.[3]

Tetrachlorethane is a colorless, heavy, refractive liquid, of chloroform-like odor, practically non-hygroscopic, of slight volatility and high boiling point, which renders its recovery after use a matter of simple distillation. It has a specific gravity of 1.6208 at 4°/4°; 1.603 at 17°/17°;[4] commercial tetrachlorethane ranging in gravity from 1.595-1.60 at 15°.[5] The boiling

1. F.P. 420489, 1910; abst. C.A. 1912, **6**, 1981; J.S.C.I. 1911, **30**, 307; Chem. Tech. Rep. 1911, **35**, 259. U.S.P. 1030916, 1912; abst. Mon. Sci. 1913, **78**, 7. E.P. 2375, 1911; abst. J.S.C.I. 1911, **30**, 982; C.A. 1911, **30**, 3326. Swiss P. 55752, 1911; D.R.P. 241559, 1909; abst. C.A. 1912, **6**, 1291. Aust. P. 55443, 1911; abst. Zts. ang. Chem. 1912, **25**, 2446; Mon. Sci. 1913, **78**, 89.

2. On account of the fact that acetylene tetrachloride is a good solvent for chlorine and a bad solvent for acetylene, it is necessary to apply the inlet pipe for the acetylene below the level at which the chlorine is admitted, so that the acetylene as it rises will always meet acetylene tetrachloride saturated with chlorine, with which it will immediately combine under the influence of the iron present, to form acetylene tetrachloride. In this manner two temporarily distinct reactions occur, firstly, the dissolution of the chlorine in acetylene tetrachloride, and secondly, the action of the acetylene on the solution in the presence of iron. The heat generated by the reaction is removed by cooling. The acetylene tetrachloride produced passes away through an overflow pipe.

3. Konsortium f. Elektrochemische Industrie, F.P. 425327, 1910; abst. J.S.C.I. 1911, **30**, 923; Mon. Sci. 1913, **78**, 119; C.A. 1912, **6**, 1981. E.P. 18602, 1904; abst. J.S.C.I. 1905, **24**, 150. E. Hoefer and M. Mugdan, U.S.P. 985528, 1911; abst. J.S.C.I. 1911, **30**, 446; Chem. Tech. Rep. 1911, **35**, 259; C.A. 1911, **5**, 1500. See also G. Koller, E.P. 15288, 1910; abst. C.A. 1911, **5**, 3351; J.S.C.I. 1911, **30**, 967; Chem. Tech. Rep. 1911, **35**, 587. Seventh International Congress of Applied Chemistry; abst. J.S.C.I. 1909, **28**, 719.

4. H. Veley, Proc. Roy. Soc. 1910, **82**, 218-19; abst. J.S.C.I. 1910, **29**, 233; C.A. 1910, **4**, 1316; Chem. Zentr. 1910, I, 1275; Bull. Soc. Chim. 1911, (4), **10**, 170; Jour. Chem. Soc. 1910, **98**, i, 214. W. Herz and W. Rathman, Chem. Ztg. 1912, **36**, 1417; abst. Chem. Zentr. 1913, I, 229; J.C.S. 1913, **104**, i, 695; ii, 26; C.A. 1913, **7**, 1318, 3866), give the following density figures, compared with water at 4 deg.; 15 deg., 1.6015; 25 deg., 1.5881; 35 deg., 1.5729; 45 deg., 1.5579; 60 deg., 1.5353; 75 deg., 1.5126; 90 deg., 1.49.

5. Mean determinations of twelve samples from five separate

point is stated by Veley to be 1.4Z2° (corr.).[1] It dissolves in water at 15° less than 0.2% by volume, and is miscible in any proportion with methyl, ethyl or amyl alcohols, ethyl or amyl acetates, petroleum benzine, benzene, toluene or xylene, chloroform and other substituted methanes, ethanes and ethylenes, and is non-inflammable.

Tetrachlorethane dissolves dammar, sandarac and mastic readily, is a poor solvent of orange and bleached shellac, an excellent solvent of castor and many other vegetable oils, and dissolves the kauri copals in large amounts, especially upon the application of a gentle heat. It has strong bactericidal action and is an effective disinfectant. It is a non-solvent of the cellulose nitrates both of high and low nitration, although tetrachlorethane is a valuable ingredient in nitrocellulose mixtures, appearing to exert an effect similar to that induced by the presence of amyl alcohol, i. e., the resplendency, luster and smoothness of the film is increased. And, although a high-boiling nitrocellulose non-solvent, there is but little evidence of precipitation. For instance a mixture of 65 parts commercial acetone (b. pt. 56°) and 35 parts (by weight) of tetrachlorethane (b. pt. 147°) will dry to a clear and tough film without any external evidence of precipitation. It therefore is a valuable adjunct as a constituent of pyroxylin mixtures, its value heretofore having been imperfectly appreciated; is a direct substitute for refined fusel oil in pyroxylin mixtures at less than one-half the cost per volume.

Tetrachlorethane is an excellent solvent for a wide range of cellulose acetates of partial hydration, its solvent action being increased by the presence of methyl, or preferably ethyl alcohol. It is especially applicable as a solvent for those cellulose acetates which have been partially hydrated, in which the hydration has not been carried to a solubility in absolute acetone, but has been carried beyond a ready solubility in sources.

1. Distillation of eight samples of one liter each in 4-bulb Ladenburg fractionation flask, each distillation occupying approximately four hours gave the following results, the per cents. being by volume: 0-140 deg., 3.6 per cent.; 140-144 deg., 3.3 per cent.; 144-145 deg., 6 per cent.; 145-146 deg., 26 per cent.; 146-146.4 deg., 24 per cent.; 146.4-147 deg., 34 per cent. Above 147 deg., 3 per cent.

chloroform. Tetrachlorethane will apparently dissolve a wider range of cellulose acetates than any other single solvent, and when ethyl alcohol, acetone, or the higher ketones are added in relatively small amounts, the solvent action is considerably increased. Apparently 20 parts of alcohol to 80 parts tetrachlorethane, both by volume, gives the most satisfactory mixture for photographic and general work. Zymene is the commercial name for a mixture of tetrachlorethane and methyl alcohol in about the ratio of 5 to 3, while Solvace consists of tetrachlorethane and rectified light acetone oil (methyl-ethyl ketone primarily). Lederer[1] first patented the use of tetrachlorethane as a cellulose acetate solvent and plastic-inducing body, his preferred formula being one part of cellulose acetate to nine parts acetylene tetrachloride (whether by volume or by weight not stated). However, such a lacquer in addition to being unduly expensive, would be entirely too slow drying for commercial work, and the cost would be reduced by the introduction of commercial 100% benzol, and the speed of evaporation increased by the addition of lower boiling liquids as methyl or ethyl alcohol or acetone. Lederer has also described plastic combinations of chloral hydrate and chloral alcoholate with tetrachlorethane[2] applicable equally well to nitrocellulose, acetylated nitrocellulose, or cellulose acetate. In a cited formula, 20 parts of nitrocellulose or acetylated nitrocellulose and 15 parts of chloral hydrate is brought into solution by means of 100 parts acetone, and a mixture of 10 parts

1. D.R.P. 157379, 1904, abst. Chem. Ind. 1906, **29**, 559; Chem. Centr. 1906, II, 1544; Jahr. Chem. 1905-08, II, 984; Mon. Sci. 1908, **68**, 43; Zts. ang. Chem. 1907, **20**, 2045; Wagn. Jahr. 1906, II, 512. D.R.P. 188542, 1905; abst. Mon. Sci. 1910, **72**, 77; Chem. Zts. 1907, **6**, No. 258; Chem. Zentr. 1907, II, 1815; Jahr. Chem. 1905-08, II, 984; Wagn. Jahr. 1907, II, 404; Chem. Ind. 1907, **30**, 534. F.P. 352897, 1905; abst. J.S.C.I. 1905, **24**, 978, 984; Mon. Sci. 1907, **66**, 33. E.P. 6751, 1905; abst. J.S.C.I. 1906, **25**, 326. U.S.P. 804960, 1905; abst. J.S.C.I. 1905, **24**, 1314. Belg. P. 195840, 1906.

2. D.R.P. 152111, 1902; abst. Zts. ang. Chem. 1904, **17**, 1250; Chem. Centr. 1904, II, 382; Mon. Sci. 1910, **73**, 159; Jahr. Chem. 1904, 1168. D.R.P. 189703, 1902, being addition to D.R.P. 152111; abst. Chem. Zts. 1907, **6**, No. 387; Chem. Zentr. 1907, II, 1822; Mon. Sci. 1910, **73**, 159. D.R.P. 220228, 1907; abst. Chem. Tech. Rep. 1910, **34**; Chem. Zts. 1910, **9**, 1934; Chem. Ind. 1910, **33**, 271. F.P. 377010, 1907; abst. J.S.C.I. 1907, **26**, 1027; Mon. Sci. 1908, **68**, 444. E.P. 9537, 1907; abst. J.S.C.I. 1908, **27**, 589.

cellulose acetate in 50 parts of acetylene tetrachloride added The entire mixture is then suitable as a cellulose ester plastic or as a coating material.

In 1912 there was issued to W. Walker on a United States Patent application filed Oct. 23, 1905, patent protection for the use of acetylene tetrachloride as a cellulose ester solvent,[1] this patent being the subject of a divisional application of which the other portion issued in 1911 included the use of acetylene tetrachloride in conjunction with wood alcohol.[2] Wood alcohol, while a non-solvent of acetylated cellulose, at the same time is an advantageous addition to a liquid of high boiling point and relative low volatility as acetylene tetrachloride, because the solution thus produced dries more quickly and with uniformity. As the proper ratio between acetylene tetrachloride and wood alcohol for powerful solvent effect, the patentee produces a solution suitable for lacquer and varnish purposes by dissolving cellulose acetate in 10-12 parts acetylene tetrachloride, by weight, containing one part of wood alcohol. The author's experience is that the most powerful solvent combination is very close to their molecular weights, which is approximately 1 part of methyl alcohol to 5 parts tetrachlorethane (both by weight) or about one volume of wood alcohol to 3-3.5 volumes of tetrachlorethane.

In a French patent issued to A. Eichengruen in 1910[3] and an addition thereto of the same year,[4] the use of acetylene

1. U.S.P. 1035108, 1912; abst. Mon. Sci. 1913, 79, 110.

2. U.S.P. 1009116, 1911; abst. J.S.C.I. 1911, 30, 1447. F.P. 417319, 1910; abst. J.S.C.I. 1911, 30, 19. Tetrachlorethane appears to be the best solvent of that degree of acetylated cellulose which is soluble with difficulty in chloroform, the solubility being materially increased by the addition of ethyl alcohol. The addition of ethyl alcohol will materially improve its dissolving power for this form of acetylated cellulose. Acetone will usually precipitate cellulose acetate from such a tetrachlorethane solution.

3. E.P. 27258, 1910; abst. J.S.C.I. 1911, 30, 1112. F.P. 419530, 1910; abst. J.S.C.I. 1911, 30, 205. First Add. No. 13237, dated Sept. 29, 1911, to F.P. 419530, 1910; abst. J.S.C.I. 1911, 30, 415.

4. First Add. No. 13237, dated Sept. 29, 1911, to F.P. 419530, 1910; abst. J.S.C.I. 1911, 30, 415. In Belg. P. 259277, 1914; abst. Kunst. 1914, 4, 238, the Akt.-Ges. f. Anilin Fabrikation describe solvent mixtures of tetrachlorethane and amyl alcohol, as especially useful for lacquer manufacture with cellulose acetate or acetonitrate.

tetrachloride with or without alcohol is described in the preparation of celluloid substitutes in combination with phenol and chloral hydrate. Pyridine in conjunction with tetrachlorethane has been advocated as a cellulose acetate solvent,[1] the proportions being pyridine 0.5-1%, tetrachlorethane 93.5-87%, and cellulose acetate 6-12%. This lacquer is claimed as especially suitable for cable and wire insulation. The pyridine is added as an ant-acid. A 10% solution of commercial cellulose acetate in tetrachlorethane as an uninflammable and impermeable coating material for fabrics has been patented in France.[2] L. Lederer[3] prepares artificial silk cheaper than acetate silk, and of no greater inflammability, by mixing (say) 6 parts trinitrocellulose, 2 parts triacetylcellulose, 27 parts acetone and 16 parts tetrachlorethane, thus making a homogeneous solution which may be projected through capillary orifices into filaments and the inflammability removed by subsequent denitration. P. Bary has described the general uses of acet-

A. Blavinhac (F.P. 460807; abst. Kunst. 1914, 4, 97) preserves wood by injection with trichlorethylene and tetrachlorethane.

1. Societe Debauge et Cie, F.P. 418347, 1909; abst. J.S.C.I. 1910, 29, 1117; 1911, 30, 96. Add. No. 15217 of F.P. 418347; abst. J.S.C.I. 1912, 31, 651; Kunst. 1912, 2, 316. For furniture polish of tetrachlorethane 55-65, penta- or tetra- chlornaphthalenes 75, cresolformaldehyde condensation product 40-55, and benzene, di- or trichlorethylene 80-120 parts, see J. Aylesworth, U.S.P. 1090440, 1914; abst. C.A. 1914, 8, 1647.

2. F.P. 427562, 1910; abst. J.S.C.I. 1911, 30, 1053; Mon. Sci. 1913, 78, 23.

3. E.P. 11625, 1909; abst. J.S.C.I. 1909, 28, 1030. F.P. 402-072, 1909; abst. J.S.C.I. 1909, 28, 1221. D.R.P. 240751, 1908; abst. C.A. 1912, 6, 2179; Kunst. 1912, 2, 15; Chem. Zentr. 1911, II, 1843. D.R.P. 248559, 1909, Add. to D.R.P. 240751, 1908; abst. Kunst. 1912, 2, 296; Zts. ang. Chem. 1912, 25, 1884. For manufacture of acetylene tetrachloride-soluble cellulose acetate with chloracetic acid, see E.P. 14255, 1906; abst. J.S.C.I. 1907, 26, 220. F.P. 368-738, 1906; abst. J.S.C.I. 1907, 26, 30. D.R.P. 198482, 1905; abst. Mon. Sci. 1911, 74, 54; Zts. ang. Chem. 1908, 21, 1760; Chem. Zentr. 1908, II, 118; Jahr. Chem. 1905-08, II, 982; Chem. Ind. 1908, 31, 378. In the use of tetrachlorethane it is advisable to distil the commercial product to remove the water therefrom. This may readily be accomplished by distilling the tetrachlorethane until it fractionates clear, and then using the portion which has not distilled, which will be usually about 90% of the total. The cellulose acetate to be dissolved should be dried until the normal moisture content of about 4% is reduced to less than 0.5%. In this manner it is possible to produce more resplendent cellulose acetate films, and to add a larger proportion of non-solvent as benzol to the solution without injuriously affecting the strength of the film.

ylene tetrachloride in connection with cellulose acetate.[1] E. Berl,[2] L. Clement and C. Riviere,[3] E. Fischer,[4] and W. Main,[5] have given general information. The practical equipment for the manufacture of tetrachlorethane solution of cellulose acetate has been detailed by Clement and Riviere,[6] including costs and formulas.

As a solvent, acetylene tetrachloride stands to cellulose acetate in much the same relationship that amyl acetate does to cellulose nitrate. Both are the highest boiling practical solvents for the respective esters, both induce temporary plasticity, tetrachlorethane the greater, due to a higher boiling point and lower volatility. Both may be attenuated with benzine and benzene and still exert their solvent effect, but tetrachlorethane differs from amyl acetate in having its solvent power enhanced by the addition of non-solvent alcohols as methyl and ethyl and also by the fact that acetone will precipitate cellulose acetate of limited hydration from its solution in tetrachlorethane, whereas acetone will dissolve probably a wider range of cellulose nitrates than amyl acetate. The value of tetrachlorethane as a solvent may be increased by submiting the liquid to careful fractionation, distilling off the lighter and turbid portion, and using the remainder, which is practically anhydrous. By similarly artificially drying the cellulose acetate before solution, it is possible to use larger amounts of benzene and other cellulose acetate non-solvents without

1. Eighth International Congress of Applied Chemistry, vol. 9, page 9.

2. Zts. gesamte Schiess. u. Sprengst. 1909, 4, 81-83; abst. Chem. Zentr. 1909, I, 1275-76; Jahr. Chem. 1909, II, 384.

3. Le Caoutc. et la Guttap., 1911, 8; abst. Kunst. 1912, 2, 338.

4. Kunst. 1912, 2, 21-24, 48-52, 64-69; abst. C.A. 1912, 6, 2314.

5. Rev. Scien., 1912, 50, 783-86. Chemiste, 1911, 3, 41-45; abst. C.A. 1912, 6, 1849.

6. La Revue Chim. Industrielle, 1911, 22, 215-220. Caout. et Guttap., 1911, 8, 5449-50; abst. C.A. 1911, 5, 3908. L. Desvaux (F.P. 450746, 1912; abst. J.S.C.I. 1913, 32, 596) prepares a non-inflammable composition by mixing 50 k. acetone-soluble cellulose acetate with 10 k. coal tar creosote, 25 k. pentachlorethane and 25 k. alcohol until the acetate is dissolved. To the pasty mass in the mixer is added 12.5 k. previously softened gelatin, the whole being mixed with the addition of glacial acetic acid and rolled into sheets. A number of these sheets, superposed, placed in a hydraulic press and compacted, forms the finished plastic mass.

impairment in luster and smoothness of the final film. Where the maximum of benzol is used (and from matters of economy this should be always), and liquids containing variable amounts of moisture, as commercial wood alcohol and denatured grain alcohol, the total solvent mixture can be made still more anhydrous by mixing the benzene and alcohol, filtering through absorbent cotton to remove the precipitated water, then adding the tetrachlorethane to this filtered, now clear, mixture and dissolving the cellulose acetate therein. On account of lower boiling point, 100% benzol is the preferable grade to use. Warm tetrachlorethane does not seem to exert a greater solvent action than when used cold. In dissolving resins, the reverse is the case. In addition to its power as a direct solvent, tetrachlorethane is also technically valuable on account of its ability to impart plasticity, and this property has been taken advantage of in the preparation of continuous cellulose acetate films for cinematographic work. Films procurable upon the open market have been found to contain from seven to fourteen per cent tetrachlorethane. This property is also of value in the manufacture of acetate phonograph records, especially the disk records as distinguished from the circular records. Acetylene tetrachloride is not a solvent of cellulose formate or propionate. It is relatively uninflammable and noncombustible. The narcotic effect is less than carbon tetrachloride,[1] is four times more toxic than chloroform,[2] may be steam distilled without decomposition, its corrosive action on iron being less than that of carbon tetrachloride under the same conditions.

G. Convert claims [1] that upon preparing solutions of cellulose acetate in pure tetrachlorethane there will, after a while, be a distinct separation into two layers, a liquid free from cellulose acetate and a jelly of constant composition in which 100 parts of the acetate retains 720 parts of solvent. In drying

1. According to Konsortium f. Elektrochemische Industrie, Chem. Ztg. 1908, **32**, 529-530; abst. J.S.C.I. 1908, 27, 643.

2. H. Veley, Proc. Roy. Soc. 1910, **82**, 218-219; abst. J.S.C.I. 1910, **29**, 233; C.A. 1910, **4**, 1316; Chem. Zentr. 1910, **81**, ((5), 14), I, 1275; Bull. Soc. Chim. 1911, (4), **10**, 170; Jour. Chem. Soc. 1910, **98**, i, 214. A. Tschirch and W. Schmitz (Gummi. Ztg. 1912, **26**, 2079; abst. J.S.C.I. 1912, **31**, 1042) recommend tetrachlorethane and perchlorethylene as rubber solvents.

at 50° the mixture still retains 27.2 gm. solvent per 100 gms. of the cellulose acetate. The product is non-inflammable, and with that amount of tetrachlorethane in it, would possess plastic properties. In purchasing tetrachlorethane an examination for acidity, determination of specific gravity and a fractionation test is usually all that is required to determine suitability as a cellulose acetate solvent.

In the chemical industries it is further employed to purify substances through re-crystallization, the advantages being its high dissolving ability, coupled with a low volatility and wide cooling interval, i. e., the variation of about 130° between its boiling temperature renders a high percentage of precipitation of any substance saturated in tetrachlorethane at or near the boiling point. It is especially advantageous in the extraction of sulfur on account of its practically unlimited dissolving power at the boiling point, and the low solubility of sulfur therein at room temperature. In order to render it more applicable as a solvent for resins, and to neutralize any hydrochloric acid split off, organic compounds which take up HCl by saturation of adjoining carbon atoms may be added, such as turpentine oil or pinene.[1] As a fat solvent for degreasing raw wool and other fibrous materials;[2] as a detergent soap;[3] a soap compound;[4] and fluid cleaning emulsions are other industrial uses in which it has been applied. In the caoutchouc industry, its noninflammability as compared with carbon bisulfide, and neutrality in comparison with the chlorides of sulfur, are the main advantageous points.[5] The non-explosive and non-combustible properties of the chlorine-substituted ethanes combine with safety in transportation the advantage of lower freight rates with a total absence of vexatious

1. Salzbergwerk Neu-Stasfurt, D.R.P. 185374, 1905; abst. J.S.C.I. 1907, **26**, 1287; C.A. 1907, **1**, 2657.

2. Crefelder Seifenfabrik Stockhausen and Traiser, E.P. 21280, 1908; abst. C.A. 1909, **3**, 2516; J.S.C.I. 1909, **28**, 702.

3. J. Stockhausen, U.S.P. 998995, 1910; abst. C.A. 1910, **4**, 3018.

4. G. Koller, E.P. 15288, 1910; abst. C.A. 1911, **5**, 3351; J.S.C.I. 1911, **30**, 967. U.S.P. 1038900, 1912; abst. J.S.C.I. 1912, **31**, 998; C.A. 1912, **6**, 3536.

5. Frankenburg, Ltd., R. Frankenburg and F. Betteridge, E.P. 17156, 1908; J.S.C.I. 1904, **23**, 906.

restrictions.

The tests for purity of tetrachlorethane are its boiling point, specific gravity, freedom from residue upon evaporation, insolubility in water and absence of acidity. It should also be practically colorless. One cubic centimeter tetrachlorethane and 99 cc. water should not give a clear solution upon continued shaking. 10 cc. evaporated to dryness should give a residue less than 0.05 gm. The acidity upon titration with alcoholic alkali should be less than 0.5% by weight.

Pentachlorethane, C_2HCl_5, was first obtained by V. Regnault [1] by the prolonged action of chlorine on ethyl chloride, and afterwards by E. Paterno [2] by the action of phosphorus pentachloride upon chloral. T. Thorpe [3] has examined this method in detail. A more recent and commercial process is that of the Salzbergwerk Neu-Stassfurt and Theilnehmer,[4] in which pentachlorethane is formed as an intermediate product of the reaction in the conversion of tetrachlorethane to hexachlorethane by treatment with chlorine under the influence of chemically active rays of artificial light, without the aid of a chlorine carrier. As source of light, an open arc lamp or mercury vapour lamp may be used. The temperature of the liquid should not be allowed to rise above 50-60°. Pentachlorethane is obtained if the chlorination is stopped when an excess of chlorine of about 10% over the amount required to produce the pentachlor-compound has been added. The product, which consists of about 90% pentachlorethane and 10% of the hexachlor-compound, is purified by fractionation.[5]

1. Ann. 1840, **33**, 321.

2. Ann. 1869, **151**, 117; abst. Compt. rend. 1869, **68**, 450-53; Zts. Chem. 1869, 245; Chem. Centr. 1869, (2), **14**, 540; Bull. Soc. Chim. 1869, N.S. **11**, 485; Jahr. Chem. 1869, 505.

3. J.C.S. 1880, **37**, 141.

4. E.P. 1105, 1912; abst. J.S.C.I. 1912, **31**, 458; C.A. 1913, **7**, 2286. U.S.P. 1036224, 1912; abst. J.S.C.I. 1912, **31**, 901; Mon. Sci. 1913, **78**, 8. D.R.P. 248982, 1911; abst. C.A. 1912, **6**, 2824. F.P. 441249, 1912; abst. J.S.C.I. 1912, **31**, 844; Mon. Sci. 1913, **78**, 140. U.S.P. taken out in name of H. Haberland and W. Schaefer.

5. In the preparation of hexachlorethane, according to this process, the passage of chlorine is preferably stopped when the product consists of a thick paste; the white crystalline mass is then pressed, and the liquid mixed with a further quantity of tetrachlor-

Commercial pentachlorethane is a colorless, heavy, neutral, refractive liquid, of powerful odor somewhat resembling chloroform. It is prone to deposit a greenish-yellow oily layer on the sides of the container, especially when stored in a bottle exposed to the light. The specific gravity of the commercial product is about 1.673 at 15.6.[1] Thorpe gives the corrected boiling point as 159.1°, and sp. gr. at 10.15°/4° as 1.69263. Solubility in water at room temperature less than 0.2% by volume. There, however, is sufficient water in solution so that the first fractions in a distillation are always turbid.

Pentachlorethane is a non-solvent of the cellulose nitrates, yet the addition of as small amount as 5% by volume in a nitrocellulose solution will increase the pliability and flexibility of the product left upon evaporation of the solvent. Its high boiling point and low volatility induces temporary plasticity in combination with other solvents. Alone it has but slight solvent action upon the chloroform-soluble cellulose acetates, and practically none upon the acetone-soluble. With both the solvency is much more pronounced upon the addition of alcohol, and in this respect it resembles tetrachlorethane and chloroform. It is a significant fact that whereas trichlorethane and pentachlorethane are practically devoid of direct solvent power for the cellulose acetates, the intermediate member (tetrachlorethane) has so pronounced solvent powers.

D. Reid [2] prepares relatively thin acetylcellulose sheets which are transparent and suitable for photographic film supports by the use of acetone and an amount of pentachlorethane

ethane and again chlorinated.

6. Mean of eight determinations taken by author. W. Herz and W. Rathman (Chem. Ztg. 1912, **36**, 1417; abst. Chem. Zentr. 1913, I, 229; J.C.S. 1913, **104**, i, 695; ii, 26) give the following density figures, compared with water at 4 deg.; 15 deg., 1.6846; 25 deg., 1.6712; 35 deg., 1.6566; 45 deg., 1.6420; 60 deg., 1.6205; 75 deg., 1.5987; 90 deg., 1.577.

1. Mean of eight determinations taken by author. W. Herz and

2. U.S.P. 1095999, 1914; abst. J.S.C.I. 1914, **33**, 640; C.A. 1914, **8**, 2124.

equal to 50-100% of the weight of the cellulose ester used.

H. Dreyfus employs pentachlorethane in the manufacture of noninflammable plastic masses[1] in connection with that type of cellulose acetate which is insoluble or sparingly soluble in tetrachlorethane alone, but readily soluble on the addition of alcohol. As an example, 80 kilos of cellulose acetate are ground with 40 liters each of alcohol and pentachlorethane, or 40 kilos of cellulose acetate are ground with 20 liters of alcohol and 20 liters of pentachlorethane, to which is added 5 kilos of mannol. This proportion of pentachlorethane and alcohol is materially different from that found most suitable by W. Lindsay,[2] who prefers equal volumes of pentachlorethane and methyl alcohol. Inasmuch as the specific gravity of pentachlorethane and methyl alcohol is approximately 2 to 1, it follows that the prescribed formula of Lindsay is about 1 volume of pentachlorethane to 2 volumes of methyl alcohol. Methyl alcohol is preferable to ethyl alcohol as an adjunct to pentachlorethane as a cellulose acetate direct solvent, the substitution of a small amount of acetone in the methyl alcohol apparently materially increasing the solvent effect. A mixture of tetrachlorethane, pentachlorethane, substantially anhydrous acetone and 98% wood alcohol, produces a mixed solvent of a wide range of application depending upon the manipulation of the quantities of one or the other of the included fluids. Furthermore such a mixture has the advantage of containing direct cellulose acetate solvents of variation in boiling points from 56 to 147°.

In another process[3] pentachlorethane in combination with acetone is advocated, the process being more fully illustrated by the following two examples: 200 parts of cellulose acetate[4] are mixed with 100 parts pentachlorethane and 700 parts

1. F.P. 432047, 1911; abst. J.S.C.I. 1912, **31**, 24; E.P. 20976, 1911. Belg. P. 241252, 1911. The Salzbergwerk Neustassfurt (D.R.P. 248982, 1911) have described a method of preparing pentachlorethane and hexachlorethane by the action of ultra violet rays in the chlorination of tetrachlorethane.

2. U.S.P. 1041112, 1912; abst. Mon. Sci. 1913, **79**, 110.

3. E.P. 14364, 1910; abst. J.S.C.I. 1910, **29**, 1152. Aust. P. 46991, 1910. Swiss. P. 52438; abst. Kunst. 1912, **2**, 135. D.R.P. Anm. F.-28111, Aug. 25, 1909. F.P. 417250, 1910; abst. J.S.C.I. 1911, **30**, 19.

4. Prepared according to E.P. 24067, 1906; abst. J.S.C.I. 1907,

of acetone, the filtered solution when poured on plates leaving flexible films, the flexibility depending upon the proportion of pentachlorethane to acetic ester. Or, 120 parts of cellulose acetate[1] are dissolved in a mixture of 100 parts of pentachlorethane, 130 parts of alcohol and 650 parts of chloroform. In a third example the solution of 200 parts of cellulose acetate in a mixture of 150 parts of ethyl alcohol and 500 parts of pentachlorethane is stipulated. While not so stated by the patentees, it is apparent that in the above examples, parts by volume is intended. The use of pentachlorethane and alcohol has also been described by the Eastman Kodak Company.[2]

The advantageous points in the selection of pentachlorethane are slow volatility, entire absence of hygroscopicity, high boiling point and insolubility in water, coupled with a miscibility in any proportion with the usual liquids entering into cellulose acetate mixtures.

Hexachlorethane (Carbon trichloride, Perchlorethane), may be prepared as the end product in the chlorination of ethyl chloride,[3] or ethylene chloride;[4] from acetylchloride with excess of phosphorus pentachloride to 180°;[5] or from propyl chloride with an excess of iodine trichloride to 200°.[6] F. Michel[7] prepares hexachlorethane by leading chlorine gas

26, 1213. F.P. 371447, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci. 1908, **68**, 79; Chem. Tech. Rep. 1907, **31**, 149.

1. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, **60**, 173. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci. 1903, **60**, 54. Aust. P. 31391. It. P. 62042, 1901.

2. F.P. 408396, 1909. See E. Rousseau, F.P. 436100, 1911; abst. J.S.C.I. 1912, **31**, 410.

3. A. Laurent, Ann. Chim. Phys. 1837, (2), **64**, 328.

4. Faraday, Ann. Chim. Phys. 1821, (2), **18**, 48. A good yield of perchlorethane is obtained by the action of aluminum amalgam on carbon tetrachloride at 70°, according to K. Hofmann and E. Seiler, Ber. 1905, **38**, 3058; abst. Jahr. Chem. 1905-08, II, 140; Chem. Centr. 1905, II, 1229.

5. H. Huebner and F. Mueller, Zts. fur. Chem. 1870, **13**, 328,

into a mixture of sulfur chloride and reduced iron, boiling under reflux condenser and crystallizing the cooled liquid for seperation of the hexa-derivative. They are purified by steam sublimation, drying and recrystallization from alcohol. The Societe Leduc, Heitz et Cie prepare a cellulose acetate plastic by combining 19% each *b*-naphthol and hexachlorethane with cellulose acetate. Such a combination is especially useful, the inventors claim, as a lacquer for wire insulation and for the impregnation of thin papers.[1] Hexachlorethane consists of white crystals, practically insoluble in water, readily soluble in alcohol, ether, chloroform and acetylene tetrachloride. Alone it is nonsolvent of all forms of acetated cellulose. In methyl alcohol or acetone, it gelatininzes acetylcellulose upon the application of heat, and has been used [2] to increase the viscosity of cellulose ester solutions.

Benzine (petroleum ether) and **Benzene** (benzol) are hydrocarbon nonsolvents and anhydrous diluents, used either in the attenuation of the acetating mixture in order to preserve the original structural form of the cellulose during esterification, or to reduce the temperature of the esterizing bath by the introduction of non-reacting fluids. The benzine employed is preferably of 62° Be. grade, and the benzene, either the so-called pure, or 100%, the latter meaning that 100% of the mixture (or all of it) will distil at or under the temperature of boiling water. Before the automobile consumed such enormous quantities of the petroleum benzines, the cost was so low and the grade so constant that benzine was used in preference to the coal tar benzols as non-hygroscopic cellulose ester diluents, but the amount of benzine used in this industry has steadily declined within the past few years, being superceded by the benzols and toluols. While this change is partly attributable to the rise in cost of benzine,

Chem. Centr. 1870, 418; Jahr. Chem. 1870, 437; Bull Soc. Chim. 1870, (2), **14**, 229.

6. F. Krafft and V. Merz, Ber. 1875, **8**, 1298; Chem. Centr. 1875, 757; Jahr. Chem. 1875, 245; Bull. Soc. Chim. 1876, **26**, 76; J.C.S. 1876, **30**, 539.

7. Zts. ang. Chem. 1906, **19**, 1095; abst. J.S.C.I. 1906, **25**, 713.

1. F.P. 429788, 1911; abst. J.S.C.I. 1911, **30**, 1267.

2. F.P. 418347, 1909; abst. J.S.C.I. 1911, **30**, 96. First Add.

it is mainly due to the fact that the consumer has discovered that both cellulose nitrates and cellulose acetates in solution may be diluted with larger volumes of benzene than with benzine without subsequent precipitation or impairment of the luster or resplendency of the formed ester film. Over twice the volume of benzene 100% can be added to a cellulose ester solution without precipitation of the ester, as compared with benzine.

Benzine 62° is not miscible with commercial wood alcohol, denatured grain alcohol or glacial acetic acid; miscible in all proportions without turbidity with acetone, tetrachlorethane, refined fusel oil, benzol 100%, toluol, xylol or oil of turpentine. If benzine is not miscible with the above to a clear solution, the latter contain undue amounts of water therein. When benzine is used in the acetating mixture either to modify speed of acetation or dilute the acetylizing fluid so the cellulose does not pass into solution, the boiling point should be removed as far as possible from that of acetic acid and anhydride, to facilitate subsequent recovery and seperation by fractionation. Benzine 72° boils at a considerably lower temperature than either acetic acid or anhydride, and is unaffected by them.

Benzol is a commercial name applied to liquid aromatic hydrocarbon mixtures derived from coal tar light oil. Crude benzol consists largely of benzene, toluene and the three xylenes. The two former being available in chemically pure form in the United States, no attempt is made to separate the three xylenes. 100% benzol, 90% benzol, and 50% benzol are mixtures of benzene, toluene and xylene, their percents indicating amounts distilling under 100°. Solvent naphtha contains mainly xylenes and cumenes. All the above products are found in the market both in the straw colored form and in the purified, or water-white condition. All contain unsaturated compounds, benzol being the result of distillation to remove empyreumatic matters and naphthalenes.[1] In nitrocellulose

14217, to F.P. 418347; abst. J.S.C.I. 1912, 31, 651; Kunst. 1912, 2, 316.

1. J. Weiss, Jour. Ind. Eng. Chem. 1911, 3, 10; abst. C.A. 1911, 5, 1507.

solutions the limit of benzine to amyl acetate for a solvent mixture is about 55% benzine, whereas about 70% benzol may often be used. Benzol 100% is always preferable on account of its lower boiling point and greater speed of evaporation. The solubility of water in benzol at 22°, according to W. Herz, is 0.72%,[1] and 0.61% at 23°, according to E. Grosshuff.[2] The sp. gr. of benzene is 0.89993 at 0°,[3] 0.8844 at 15°,[4] 0.8799 at 18.1°,[5] 0.878434 at 20°,[6] and 0.87368 at 25°.[7] Poisoning with benzol has been attributed to minute traces of nitrobenzene contained therein.[8] D. Stavorinus[9] and J. Weiss[10] have devised methods for estimating carbon bisulfide in commercial benzenes. The inflammability may be materially reduced by the introduction of carbon tetrachloride,[11] or tetra-

1. Ber. 1898, **31**, 2669; abst. J.C.S. 1899, **75**, ii, 83.
2. Zts. Elaktrochem, 1911, **17**, 348; abst. C.A. 1911, **5**, 2550.
3. Biron, Jour. Soc. Phys. Chem. 1910, **42**, 147; abst. J.C.S. 1910, ii, 394.
4. Tyrer, J.C.S. 1910, **97**, 2624.
5. Walden, Zts. physik. Chem. 1910, **75**, 560.
6. Polowzow, Zts. physik. Chem. 1910, **75**, 520.
7. De Leeuw, Dissertation, Amsterdam, 1910, p. 22.
8. H. Wichern, Munch. med. Woehschr, 1909, **56**, 11; abst. C.A. 1909, **3**, 797. E. Johnson, J.A.C.S. 1906, **28**, 1200; abst. J.S.C.I. 1906, **25**, 955. C. Glaser, J.S.C.I. 1911, **30**, 519.
9. Jour. Gasbeleucht, 1906, **49**, 8; abst. J.S.C.I. 1906, **25**, 139. For manufacture of benzene in Russia, see N. Pantjuehow, Rigaer Ind. Zeit. 1902, **28**, 217; abst. Chem. Zts. 1902, **26**, 317; J.S.C.I. 1902, **21**, 1449. For deodorization of benzene and benzine, see Pharm. Post, **33**, 639; abst. J.S.C.I. 1901, **20**, 238.
10. Jour. Ind. Eng. Chem. 1909, **1**, 604; abst. J.S.C.I. 1909, **28**, 974. H. Hirzel (U.S.P. 991205, 1911; abst. C.A. 1911, **5**, 2326) has described a benzene recovery plant. For composition of commercial benzene, see M. Rakusin, Mat. gras. 1909, 1308, 1346. Chem. Ztg. 1907, **31**, 6. Caout. et Guttap. 1908, **5**, 2504; abst. J.S.C.I. 1907, **26**, 86; 1909, **28**, 17; 1912, **31**, 891; C.A. 1909, **3**, 711, 1081. For apparatus for testing benzine, see C. Roth, E.P. 21518, 1905; abst. J.S.C.I. 1906, **25**, 236. For testing varnish-makers' benzine, see Chem. Ztg. 1912, **35**, 1374; abst. C.A. 1912, **6**, 1072. For discussion of various names of benzine and benzene, see H. Schelenz, Zts. ang. Chem. 1908, **21**, 2577; abst. C.A. 1909, **3**, 882.
11. J. Lyndall and K. Costley-White, E.P. 16756, 1904; abst. J.S.C.I. 1905, **24**, 962. See Le Petrole, through Chem. Tech. Rep. 1913, **31**, 8; abst. C.A. 1913, **7**, 1804. For purifying and decolorizing benzine, see Martini and Huneke Maschinenbau, F.P. 445866, 1912; abst. J.S.C.I. 1912, **31**, 1177. For flash, fire and explosion tests of benzine (naphtha), see E. Barrier, J. Ind. Eng. Chem. 1910, **2**, 16; abst. C.A. 1910, **4**, 669. For long article on the manufacture of benzine, see E. Wild, Petroleum, 1913, **8**, 668; abst. J.S.C.I. 1913, **32**, 277; C.A. 1913, **7**, 2679. For solubility of water in benzene and

chlorethane, or by cholorination.[1] Commercial benzene has been used in the separation of cellulose esters,[2] as a precipitant for acetated cellulose,[3] as a medium in the presence of which to acetylate cotton,[4] and as a diluent in esterizing.[5]

light petroleum oil, see E. Groschuff, Z. Elektrochem. 1911, 17, 348; abst. J.S.C.I. 1911, 30, 608.

1. E. Barboni, F.P. 350313, 1904; abst. J.S.C.I. 1906, 25, 117.

2. U.S.P. 902093, 1908; abst. J.S.C.I. 1908, 27, 1130. E.P. 26501, 1906; abst. J.S.C.I. 1907, 26, 430. F.P. 371356, 1906; abst. J.S.C.I. 1907, 26, 340; Mon. Sci. 1908, (4), 68, 79. D.R.P. 185151, 1905; abst. Zts. ang. Chem. 1907, 20, 1541; Chem. Zentr. 1907, 78, 498; Jahr. Chem. 1905-08, I, 984.

3. E.P. 7341, 1903; abst. J.S.C.I. 1904, 23, 501. F.P. 330714, 1903; abst. J.S.C.I. 1903, 22, 1100; Mon. Sci. 1904, (4), 60, 66. Toluene and xylene are also non-solvents.

4. U.S.P. 812098, 1906; abst. J.S.C.I. 1906, 25, 232; Mon. Sci. 1906, (4), 64, 120. E.P. 24083, 1904; abst. J.S.C.I. 1905, 24, 1081. F.P. 347906, 1904; abst. J.S.C.I. 1905, 24, 454; Mat. Color, 1905, 9, 147; Mon. Sci. 1906, (4), 64, 15; Chem. Ztg. 1905, 29, 493. D.R.P. 184145, 1904; abst. Chem. Zentr. 1907, 78, 365; Mon. Sci. 1909, (4), 70, 77; Jahr. Chem. 1905-08, 983; Zts. ang. Chem. 1908, 21, 268; Chem Ind. 1907, 30, 238. D.R.P. 184201, 1904; Zts. ang. Chem. 1908, 21, 268; Chem. Zentr. 1907, 78, 365; Mon. Sci. 1909, (4), 70, 77; Jahr. Chem. 1905-08, 984; Chem. Ind. 1907, 30, 257. Aust. 35015. Belg. P. 182216, 1905; Swed. P. 20249, 1905. Russ. P. 11492, 1907.

5. U.S.P. 854374, 1907; abst. J.S.C.I. 1907, 26, 713; Mon. Sci. 1907, (4), 66, 159; C.A. 1907, 1, 2316. For the preparation of cellulose acetate insoluble in benzene, see D.R.P. 222450, 1908; abst. J.S.C.I. 1910, 29, 811; Zts. ang. Chem. 1910, 23, 1389; Wagn. Jahr. 1910, 56, II, 434; Chem. Zentr. 1910, 81, 48; Chem. Zts. 1910, 9, 1902; C.A. 1910, 4, 2875. For the action of mixed alcohol and benzine on cellulose acetate, see U.S.P. 1015155, 1912; abst. Mon. Sci. 1912, 77, 163. Swiss P. 52437; abst. Kunst. 1912, 2, 135. Aust. P. 47889.

CHAPTER IV.

COMMERCIAL APPLICATION OF THE UNINFLAMMABLE CELLULOSE ESTERS.

The inflammability, combustibility and explosiveness of the higher cellulose nitrates, coupled with the variety and value of the commercial products in which they wholly or partially enter, have naturally directed attention to attempts to conserve the desirable technical properties, while at the same time eliminating substantially the tendency to ready flammability. For this reason the entire field of the nitrocellulose industry has been invaded by the cellulose esters in endeavors to replace pyroxylin, celluloid and the collodions by the difficultly burnable acetylated celluloses. In many of these instances the peculiar property of thermo-plasticity, so highly developed in celluloid, was evident only in a diminished degree in the corresponding acetates, which hampered the acetic esters from fields in which they otherwise would find many uses. The greater cost of production of the acetic esters was a barrier to technical development where competition due to price was the prime factor. A well marked tendency to brittleness in cold weather has also been a point of imperfection that is not apparent with the pyroxylin plastics. From a theoretical viewpoint the acetic esters of cellulose have had a peculiar interest, in that they furnished an entirely different point of attack in endeavors to elucidate the inner structure of the cellulose aggregate.

It appears quite probable that the cellulose acetates will never be able to successfully compete with the nitrated celluloses where cost of production is the main factor, but rather that their uses will be restricted to those fields where their specific properties of non-inflammability, resistance to mercerization, faint affinity for cotton dyestuffs, absence of notable

tendering in the wetted condition, and low specific conductive capacity, counterbalance increased cost of production. The manufacturing costs hinge upon the price of acetic anhydride and effective methods for its recovery from the acylating bath.

Cellulose Acetate Plastics. The ever-increasing uses to which the pyroxylin plastics typified by celluloid are put has resulted in continuous experimentation in endeavors to produce cellulose acetate plastics which would conserve the excellent plasticity of celluloid with the decreased inflammability of the acetylcelluloses. The combination of the desirable essentials of incombustibility with a low plasticity and ability to produce moldable forms has, as yet, not been brought to the desired state of perfection. The first step in this direction was the physical admixture of cellulose nitrates and acetates in various proportions to reduce the inflammability and to conserve the thermo-plasticity. E. Zuehl[1] combines cellulose nitrate 70, cellulose acetate 30, with camphor 50 parts. L. Lederer makes use of the mutual solvent chloral, either as hydrate or alcoholate,[2] preferring to first mix 2 parts of chloral hydrate with 5 parts nitrocellulose, and to add to this a mixture of 3 parts acetylcellulose with 2 parts chloral alcoholate. Such a formula, however, is unduly expensive. Unsaturated hydroaromatic ketones, as carvone, pulegone or cyclohexanone, have been advocated, a satisfactory formula being stated as follows: 100 parts of cellulose acetate is first heated for some hours with 55 parts of benzyldihydrocarvone dissolved in acetone or chloroform, celluloid then being added, after which the excess of solvent is removed either by vacuum or under pressure.

1. U.S.P. 729990, 1903. Zuehl and Eisemann, D.R.P. 162239. For the role of camphor as solvent for acetylcellulose, see A. du Bosc, Caout. et Guttap. 1913, **10**, 7011; abst. Kunst. 1913, **3**, 352. For non-inflammable celluloid recipes, see Rev. chim. ind. 1909, **20**, 82, 105; C.A. 1909, **3**, 2039.

2. E.P. 9537, 1907; abst. J.S.C.I. 1908, **27**, 589. F.P. 377010, 1907; abst. J.S.C.I. 1907, **26**, 1027; Mon. Sci. 1908, (4), **68**, 444. D.R.P. 152111, 1902; abst. Zts. ang. Chem. 1904, **17**, 1250; Chem. Centr. 1904, **75**, II, 382; Mon. Sci. 1901, (4), **73**, 159; Jahr. Chem. 1904, 1168. D.R.P. 189703, 1902, Add. to D.R.P. 152111, 1902; abst. Chem. Zts. 1907, **6**, 387; Chem. Centr. 1907, **78**, 1822; Mon. Sci. 1910, (4), **73**, 159. D.R.P. 220228, 1907; abst. Chem. Zts. 1910, **9**, 1934; Chem. Ind. 1910, **33**, 271; Chem. Tech. Rep. 1910, **34**,

The incombustible celluloid of J. Schmerber and L. Morane[1] comprised combining the cellulose nitrate and acetate by means of camphor dissolved in methyl alcohol, ethyl alcohol and acetone. Nitrobenzene is added to the mixture for the stated purpose of reducing the inflammability. The F. Bume plastic[2] and the incandescent mantle toughening composition of J. Hirsh[3] make use of cellulose acetate containing 12% each of camphor and castor oil, the solvent being methyl or ethyl alcohol. W. Lindsay has obtained patent protection for acetate plastics containing camphor, methyl alcohol[4] or ethyl alcohol[5] and triphenyl phosphate. W. Walker found that when cellulose acetate is combined with a solvent of low volatility such as phenol, thymol, cresol or some of the essential oils containing phenolic compounds, a marked degree of plasticity is imparted to the combination.[6] The preferable solvent should, like thymol, be one which melts at a temperature sufficiently low to unaffect the cellulose acetate, the action of the solvent being promoted by an uninflammable liquid as chloroform or tetrachlorethane. As the volatile solvent vaporizes, the acetate compound decreases in plasticity. C. Mijnessen[7] prepares plastic films by successively depositing acetylcellulose layers one upon another, or with alternate layers of gelatin of other supple ductile material, the cellulose acetate being rendered plastic by means of phenol.

180. Aust. P. 34908, 1908; abst. Zts. ang. Chem. 1909, **22**, 505.

1. F.P. 324121, 1902; abst. J.S.C.I. 1904, **23**, 569. E.P. 4863, 1903; abst. J.S.C.I. 1904, **23**, 382.

2. D.R.P. 210519, 1907; abst. J.S.C.I. 1909, **28**, 812; Zts. ang. Chem. 1909, **22**, 1620; Wagn. Jahr. 1909, **55**, 555.

3. F.P. 324718, 1903; abst. J.S.C.I. 1903, **22**, 620. In F.P. 452432, 1912; abst. C.A. 1913, **7**, 3663, the Soc. Anon. le Camphre produce plastic films with cellulose acetate and camphor-addition compounds.

4. U.S.P. 1041118, 1912; abst. J.S.C.I. 1912, **31**, 1075; C.A. 1912, **6**, 3518.

5. U.S.P. 1041116, 1912; abst. C.A. 1912, **6**, 3518; Mon. Sci. 1913, **79**, 110.

6. U.S.P. 774713, 1904; abst. J.S.C.I. 1904, **23**, 1159; Mon. Sci. 1905, (4), **62**, 50. U.S.P. 774714, 1904; abst. J.S.C.I. 1904, **23**, 1159.

7. U.S.P. 1005454, 1911; abst. J.S.C.I. 1911, **30**, 1249. E.P. 476, 1910; abst. J.S.C.I. 1910, **29**, 1082. F.P. 411298, 1910; abst. J.S.C.I. 1910, **29**, 978; Phot. Ind. 1910, 1221. Eders Jahr, 1911, 526. Aust. P. 50656, 1910; abst. Kunst. 1912, **2**, 77; Phot. Ind.

H. Manissadjian has patented [1] a non-inflammable celluloid substitute comprising 40 parts by weight of acetylcellulose dissolved in 100 parts of slightly warmed ethyl acetate. Castor oil to the extent of 10-20% of the weight of the solution is then added to increase plasticity. Finally there is incorporated about 15 parts glycerol di- or tri-acetate, partly to render the material more supple, and also to decrease its combustibility. In the author's experience, the amount of castor oil to acetylcellulose (14 to 28 parts castor oil to 40 parts acetylcellulose) is entirely too high, such a mixture continually exuding castor oil, and having but little strength.

L. Lederer has developed a plastic cellulose acetate containing no camphor, and in which the plasticity depends primarily upon small amounts of acetylene tetrachloride [2] still

1911, 28. Belg. P. 222106, 1910. Hung. Anm. M.-3691, Dec. 30, 1909. Swiss P. 51839, 1910; abst. Kunst. 1912, 2, 77.

1. E.P. 27201, 1908. Swiss P. 43330, 1907. Hung. Appl. M-3798, 1910. See Snowden & Co., Belg. P. 241975, 1912; F.P. 437411, 1911. Hung. Appl. S-6073, 1912. Acetylcellulose solvents, A. Wohl, Hung. Appl. 2966, 1911; W-3204, 1911; Belg. P. 241116, 1911. For plastic, solid formylcellulose solutions, consult Vereinigte Glanzstoff Fabriken, Hung. Appl. G-3096, G-3210, G-3306; Swiss P. 55942, 1911. Nitritfabrik, Akt.-Ges., Aus. Appl. 5655, 1909. Hung. Appl. K-3937. Weber and Cross, Swed. P. 10976. G. Meyer, Aust. Appl. 1793 of 1911. H. Reeser, Hung. Appl. R-2398, 1909. C. Mijnssen, Hung. Appl. M-3691, 1909. Manufacture of cellulose fatty-acid esters, Society of Chemical Industry, Basle. E.P. 21016, 1914. In F.P. 463616, abst. Kunst. 1914, 4, 293, P. Lagrange describes combinations of nitrocellulose and acetylcellulose.

2. Although acetylene tetrachloride is such an excellent cellulose acetate solvent, the chemically closely related bodies trichlorethylene and dichlorethylene are non-solvents. However, F. Bayer & Co. (E.P. 16932, 1910), have shown that dichlorethylene in admixtures with alcohols is capable of dissolving cellulose acetates. Those cellulose esters which are readily soluble in acetone are dissolved by the mixture at ordinary temperatures, while those esters soluble in chloroform, and sparingly soluble in acetone require heating for solution. Suitable proportions are stated as 650-730 parts dichlorethylene to 150 parts of alcohol. In E.P. 14364, 1910, F. Bayer & Co. describe the usefulness of pentachlorethane as a cellulose acetate liquifying agent, with addition of other dissolving or diluting fluids. While pentachlorethane alone has only a very slight dissolving action on cellulose esters, in presence of alcohol or other solvent it plays the part towards organic cellulose esters that camphor does towards nitrocellulose in celluloid, or acetylene tetrachloride towards acetylcellulose. For example, 200 parts of cellulose acetate are mixed with 100 parts of pentachlorethane and 700 parts of acetone; when the solution is filtered and poured on plates, flexible films are obtained.

remaining in the finished article. It is understood large quantities of this acetylene tetrachloride containing cellulose acetate have been produced in Rochester, N. Y., for uninflammable photographic films. Such a film examined by the author and said to have been produced at this city was found to contain 12% acetylene tetrachloride. Lederer first[1] found that when cellulose acetate is caused to react with certain groups containing hydroxyl, ketone and amide radicals, an interlocking of the molecules appears to take place, so that the resulting compounds are plastic. In a soft state impressions of etched or engraved plates may be taken on the material without difficulty, the delicate and fine points of the etching being faithfully reproduced. The invention is described as being preferably carried out in one of the following ways:

(*a*) 1 part of cellulose acetate and 1.5 parts of phenol[2] are fused at about 40-50°. As soon as a clear solution has formed the mass is placed on warm glass or metal plates and allowed to cool gradually. After standing for several days the mass, which is somewhat like caoutchouc at first, hardens into pliable sheets which can be worked or employed like celluloid.

(*b*) Another method of operation is to mix cellulose acetate intimately with one-half its weight of phenol and then subject it to great pressure. The pressed mass is then allowed to completely harden in the air.

(*c*) Or, an intimate mixture of equal parts of acetylcellulose and chloral hydrate[3] or aniline may be subjected to pressure at a temperature of 50-60°, the pressed mass being allowed to solidify in the air.

1. U.S.P. 774677, 1904; in a more recent patent (E.P. 8945, 1909) it is stated that durable softness and suppleness may be produced in cellulose acetate by the addition of a "small proportion of an organic acid ester of a monohydric phenol or of a phenol either of a homologue or nuclear substitution product of these substances."

2. D.R.P. 145106, 151918, 1902; phenol, resorcin, pyrogallol, naphthol, aminophenol, saligenin, nitrophenol, salicylic acid ester, all being claimed as efficient.

3. D.R.P. 152111, 1902. In F.P. 330714, 1903, Lederer, cellulose acetates are shaped into threads, ribbons, films, tubes, etc., by discharging thick solutions of them through suitably shaped orifices into liquids which dissolve out the solvent without dissolving the cellulose compounds. For instance, a solution of cellulose acetate in acetic acid or phenol is discharged into alcohol and the precipitated product subsequently dried. In D.R.P. 185151; abst. Jahr.

A similar method may be followed—a ketone, for instance, acetophenone—or an amide as, for example, acetamide, being employed.

The drawback with these combinations, it has been claimed, is that upon exposure to the air for a short time they materially harden and can with but great difficulty again be made plastic. The following year (1905) brought forth from Lederer a clear description of the application of acetylene tetrachloride as a combined cellulose acetate direct solvent and plastic-forming liquid [1] in which is described methods of procedure to overcome their well-known defects. The method is to bring together 1 part of cellulose acetate with 9 parts acetylene tetrachloride, stirring the mixture thoroughly until the ester has become completely dissolved. Heat may be used to facilitate solution, as acetylene tetrachloride boils at 147° and is uninflammable. For the preparation of continuous photographic films, one method of procedure would be to prepare a solution of cellulose acetate in acetylene tetrachloride as viscous as can be worked conveniently. After solution is complete, which may be facilitated by a gentle heat in a jacketed kettle, some of the solvent may be recovered by vacuum distillation, and the viscid solution after cooling worked into continuous sheets as described in Part Six under "Film Manufacture." If it is desired to produce sheets not continuous, the vacuum distillation of solvent may be carried to a point where the mass is nearly solid, which after cooling is worked under masticating rolls, pressed into blocks, seasoned and sheets planed from this matrix, as described in Part Five.

A. Lumière & Sons [2] have described non-inflammable photographic films prepared by applying to a polished surface a thin layer of cellulose acetate or other non-inflammable

Chem. 1905-08, II, 985; Wagn. Jahr. 1907, II, 403, Lederer obtains solid acetylcellulose plastic compounds by precipitating the crude ester from the acetylating bath by means of carbon tetrachloride. Compare Aust. Anm. 3060 of 1909.

1. U.S.P. 804960, 1905; F. P. 352896, 352897, 1905; D.R.P. 175379, 1904; E.P. 6751, 1905; abst. J.S.C.I. 1905, 24, 978. A process of lacquer manufacture is described where resins and cellulose acetate are combined by means of their mutual solvent, acetylene tetrachloride (tetrachlorethane). See also E.P. 26075, 1901.

2. F.P. 401228.

cellulose ester, then a layer of gelatin, and finally a photographic emulsion. The cellulose acetate layer need not be more than one-fifth to one-half the thickness of the entire film. The gelatin may have been toughened with formaldehyde, alum, etc. Films prepared in this manner are said to be unaffected in dimensions by the subsequent treatment. F. Bayer & Co. sought to obtain plasticity by the use of cellulose acetate with naphthalene, *p*-toluidinesulfamide, or a methyl ester of oxalic, phthalic or *p*-toluidine sulfonic acids, and it is stated that photographic films of considerable elasticity result from their use.

H. Reeser[1] has found that when acetylcellulose of the type which is soluble in acetone or ethyl acetate, is heated with a mixture of equal parts of benzene and ethyl alcohol, it dissolves near the boiling temperature, but separates out on cooling. If the liquid be poured off from the deposit, and camphor or a camphor substitute be added to the latter, the mixture again becomes fluid upon heating, and the product upon cooling forms a solid having plastic properties like celluloid. A practical formula for producing plastic masses according to this invention, is to heat 2 k. acetylcellulose with 20 k. each of alcohol and benzene at 60°, and then to boiling until the acetylcellulose passes entirely into solution. To the separated mass after cooling is added 600 gms. of camphor and 400 gms. of acetochlorhydrin, the whole being then heated to 50° to produce a transparent fluid which sets on cooling to a plastic mass.

In the manufacture of die and printing forms, J. Richter[2] combines acetone-soluble acetylcellulose with inadequate amounts of camphor. The Soc. Anon. Le Camphre[3] use the halogenated derivatives of camphor, preferably in conjunction with a phenol. Combinations of casein with cellulose acetate,[4]

1. Belg. P. 216668, 1909. E.P. 12976, 1909; no patent granted; abst. J.S.C.I. 1910, **29**, 147. F.P. 411126, 1909; abst. J.S.C.I. 1910, **29**, 875; Mon. Sci. 1912, **77**, 8. Aust. P. 9533, 1909. Hung. Anm. R.-2398, Dec. 23, 1909. Port. P. 7102, 1909.

2. D.R.P. 246081, 1911; abst. C.A. 1912, **6**, 2529; Chem. Tech. Rep. 1912, **36**, 323.

3. F.P. 452432, 1912; abst. J.S.C.I. 1913, **32**, 652; Kunst. 1913, **8**, 295. D.R. Anm. R.-32631, 1911.

4. E. Zuehl, U.S.P. 729990, 1903; abst. J.S.C.I. 1903, **22**, 817.

especially in the presence of phenol or chloral,[1] result in the formation of casein-acetate plastics of direct commercial interest. The cellulose ester and casein may either be dissolved by means of the common solvent, acetic acid, or the acetylcellulose in solution may be masticated with the casein, phenol or chloral, and the volatile solvent subsequently removed until the desired consistency is obtained. Anhydroformaldehyde-aniline resinate,[2] and phenol-aldehyde condensation products have been patented as efficient constituents in cellulose acetate plastics. The condensation is prepared in the initial or soluble stage, the acetylcellulose then added, and milled to a homogeneous mass. Similar are the aniline resinate-shellac combinations. Benzyldihydrocarbon and benzyldihydropulegone[3] *a*-naphthyldihydrocarbon, turpentine,[4] wax and vaseline[5] have been patented, but while they impart flexibility and a certain degree of elasticity to cellulose acetate compositions, they are almost devoid of thermoplasticity. Pyrocatchin and pyrocatechin diethyl ether,[6] especially in conjunction with the substituted chlorhydrins, combine with cellulose acetate to products of excellent plasticity. P. Leeman[7] first mixes dry casein and cellulose acetate in powder, impregnates with glacial acetic acid, and then adds small amounts of borneol or *iso*-borneol.

D.R.P. 162239, 1902; abst. Zts. ang. Chem. 1906, **19**, 498; Chem. Centr. 1905, **76**, II, 1000.

1. C. Ellis, U.S.P. 999490, 1911; abst. J.S.C.I. **30**, 1051.

2. L. Behrend, U.S.P. 952724, 1910; abst. J.S.C.I. 1910, **29**, 503. E.P. 4154, 1909; abst. J.S.C.I. 1910, **29**, 100. F.P. 402028, 1909; abst. J.S.C.I. 1909, **28**, 1212. D.R.P. 242467, 1908; abst. Kunst. 1912, **2**, 59; C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 111; Wagn. Jahr. 1912, II, 616.

3. D.R.P. 202720, 1907; abst. J.S.C.I. 1908, **27**, 1220; Zts. ang. Chem. 1908, **21**, 2428; Chem. Zentr. 1908, **79**, II, 1837; Jahr. Chem. 1905-08, II, **993**; Mon. Sci. 1912, **77**, 57.

4. F.P. 354942, 1905; abst. J.S.C.I 1905, **24**, 1169. Add. dated June 8, 1905, to F.P. 354942; abst. J.S.C.I. 1905, **24**, 1226. E.P. 12277, 12278, 1905; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185240, 1906; abst. Zts. ang. Chem. 1907, **20**, 2177; Chem. Zentr. 1907, **78**, 1037. D.R.P. 185241, 1906, Add. to D.R.P. 185240; abst. Chem. Zentr. 1907, **78**, 819.

5. F.P. 421843, 1910; abst. J.S.C.I. 1911, **30**, 415.

6. F.P. 432264, 1911; abst. J.S.C.I. 1912, **31**, 24; Kunst. 1912, **2**, 77. First Add. dated Nov. 19, 1912, to F.P. 432264; abst. J.S.C.I. 1913, **32**, 652. Belg. P. 241251, 1911.

7. Belg. P. 181194, 182050, 182051, 182052, 1905; 201017, 1907.

W. Lindsay[1] has discovered that the camphor substitutes which have a solvent action upon acetylcellulose may be broadly grouped into three classes, the first class being those substances which are non-solvents when melted, or when dissolved in either methyl or ethyl alcohol in the cold, or at room temperature, such as triphenyl phosphate, tricresyl phosphate and naphthalene. The second class embraces those substances which become solvents when melted, but are non-solvents when dissolved in ethyl alcohol at room temperatures such as camphor, tetrachlorethylacetanilid and trichlormethylacetanilid. The third class includes those substances that become solvents when melted, and also when dissolved in methyl or ethyl alcohol in equal parts by weight at room temperature. Included in this classification is toluol-sulfamid, ethyl-*p*-toluol sulfonamid, benzenesulfoamid, methyl and ethyl acetanilid. Where ethyl-*p*-toluolsulfoamid is used, the plastic may consist of 20-50 parts of this to each 100 parts acetylcellulose soluble in acetone, a sufficient amount of methyl or ethyl alcohol being added and all the ingredients incorporated into a homogeneous mass. Depending upon the fineness with which the constituents have previously been ground, the mass is allowed to remain at rest for 12-24 hours and until thorough gelatinization takes place. It then can be kneaded, masticated and otherwise treated as in the case with nitrocellulose-camphor compounds.

W. Beatty[2] combines an ester of cellulose, either the acetate or nitrate, with the condensation product of a ketone with a phenol or their homologue, or the hydroxy derivative of an aromatic hydrocarbon, dihydroxydiphenyldimethylmethane being especially suitable. The patentee advocates combining 25 parts of this material with 75 parts of cellulose acetate, the mixture being incorporated with a sufficient quantity of solvent to produce a moldable, plastic mass.

1. U.S.P. 1041113, 1912; C.A. 1912, **6**, 3517; J.S.C.I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110.

2. F.P. 447645, 1912; abst. J.S.C.I. 1913, **32**, 283; Mon. Sci. 1914, **78**, 14; Kunst. 1913, **3**, 116. Can. P. 147578, 147579, 1913; abst. C.A. 1913, **7**, 2127, 2128. Belg. P. 252594, 1913; abst. Kunst. 1913, **3**, 276. E.P. 18822, 1912; abst. J.S.C.I. 1913, **32**, 907. D.R. Anm. B.-68616, 1912; abst. Kunst. 1914, **4**, 280. Aust. P. 63966;

The acetate plastics of H. Dreyfus [1] are formed by uniting nitrocellulose or acetylcellulose, either separately or together, with one or more of the following classes of solvents—(*a*) the etherfied derivatives of the mono- or poly-phenols and their homologues in which the phenolic groups are etherified with alcohols or phenols, their homologues or substitution products such as anisol, phenetol, cresylic and naphthylic ethers, diphenyl ether, veratrole, diethylpyrocatechin ether, safrol or *iso*safrol; the chlorphenol ethers, dichlorphenols, nitroanisoles, and chlornitroanisoles (excluding trinitroanisole and trinitrophenetol which are explosive); the etherified derivatives of benzyl, such as benzyl-methyl ether; (*b*) the aromatic side-chain alcohols and substitution products such as benzyl alcohol, chlorobenzyl alcohols and the benzhydrols. Plastic compounds are said to be formed by combining the cellulose esters with one or more or the above in the presence of entirely volatile solvents such as the chlorides of carbon, acetylene tetrachloride being especially valuable in this connection.

In another process [2] is described a method of producing an acetylcellulose mass which may be moulded, blown or pressed, by the addition of relatively small amounts of camphor together with relatively large amounts of finely powdered substances, such as metal powder, asbestos, mica, graphite and similar materials. These substances are kneaded together with the acetylcellulose imxtures, and its admixtures with the acetylcellulose mixtures, and its admixtures solvent. It is claimed the mixture shows the unusual prop-

abst. Kunst. 1914, 4, 257.

1. Compare also the E.P. 20975, 1911; abst. C.A. 1913, 7, 890; Kunst. 1913, 3, 215. In F.P. 432264, 1912; abst. C.A. 1913, 7, 3414; Swiss P. 63584, 1911; abst. C.A. 1914, 8, 2252, Dreyfus claims to produce incombustible celluloid by replacing tetrachlorethane by aromatic silicon and boron compounds, which are said to possess the advantage over the phosphoric esters in not decomposing the acetylcellulose. Triphenyl borate, tricresyl borate are included. In a more recent patent (F.P. 461544, 1913; abst. Kunst. 1914, 4, 137), plastic cellulose acetate compounds are described as obtainable from the introduction of the glycerol esters of aromatic carboxyl acids. See also Can. P. 155724, 1914; abst. C.A. 1914, 8, 2927. Swiss P. 63584, 63585; abst. Kunst. 1914, 4, 216.

2. A. Eichengruen, E.P. 18189, 1910. F.P. 418744, 1911; abst. J.S.C.I. 1911, 30, 79, 798. See also E.P. 19735, 1908; D.R.P. 210519.

erty or not losing the shape and the impressions obtained under a high pressure, when repeatedly subjected to a lower pressure. This being so, these plastic masses are especially suitable for use in the graphic arts as printing and in block-printing.

Knoll & Co.[1] endeavor to overcome brittleness in acetylcellulose masses, sheets and films upon storage, by working 15% or more of zinc chloride into the acetylcellulose solution before shaping into the finished forms. The products (films, etc.) are then kept for a long time at a moderate temperature to allow of the gradual evaporation of the acetic acid, before they are washed free from impurities. For example, 100 grms. of acetylcellulose solution are mixed with 1 grm. of collodion cotton and 5 grms. of zinc chloride added, the whole being formed into films. The latter are then stored for about 3 months at about 30° before being washed.

In producing plastics by the E. Ichenhauser method,[2] the difficulties connected in the production of solid bodies by evaporation of the cellulose acetate solution are avoided by preventing evaporation of the solvent from the upper surface of the plastic solution, and permitting volatilization only from

1. D.R.P. 255704, 1911; abst. J.S.C.I. 1913, **32**, 421; C. A. 1913, **7**, 807; Kunst. 1913, **3**, 951; D.R. Anm. K.-48996, Sept. 12, 1911; Chem. Ztg. 1912, **34**, 1174. See also Knoll & Co., D.R. Anm. K.-52789; K-52025; K-48490. E.P. 16905, 1913. D.R.P. 255704, 1911. Hung. Appl. K-5168, 1912. In their D.R.P. 276013, 1912; abst. J.S.C.I. 1914, **33**, 916; Kunst. 1914, **4**, 300, white, colored or opaque objects are prepared from primary acetylcellulose solutions by the use of an aromatic ester or ether which does not decompose acetylcellulose, such as methyl-, ethyl- or *b*-naphthyl phthalates, benzyl chloride or anisol, which are added to the acetylcellulose while still in the acetylating bath or before acetylation. The resulting mixture is heated for a short time until a clear solution is obtained, when the acetylated product is precipitated in the usual manner by water, saline solutions or alcohol. White, opaque and stable filaments or films are thus formed which may be colored by the addition of suitable dyestuffs to the solution.

In D.R.P. 275962, 1911; abst. J.S.C.I. 1914, 33, 916; Kunst. 1914, **4**, 317, Knoll & Co. effect a regular and systematic reaction of cellulose with organic acids, by circulating the esterifying agent through a series of vessels containing cellulose in varying stages of acetylation, in such a manner that it comes in contact in successive vessels with cellulose in a lower state of esterification. A diluent in which the resulting ester is insoluble may be added to the esterifying agent, the presence of a catalyst being advantageous.

2. F.P. 436538, 1911; abst. J.S.C.I. 1912, **31**, 485.

the sides and bottom of the porous mold. These molds are made of unglazed earthenware or compressed fabric and are hermetically connected at their upper end with the vessel containing the solution of cellulose acetate. This container is sealed by connection with the vessel containing some of the solvent through which the air is compelled to pass, as the plastic solution is delivered into the molds. The solid body is gradually formed by evaporation into the mold, and the solution continually supplied as the body in the mold becomes concentrated.

The plastic composition of Y. Charuel[1] contains 4-25% of cellulose acetate, 60-95% of acetone and 1.5-5% of refined paper pulp, which may be either moist or dry. It is claimed to be suitable for packing joints, insulating cables or the manufacture of plates, discs, etc. Neutral bodies, such as resin, shellac or asbestos, may be incorporated for special purposes.

According to L. Grote,[2] a binding medium for making plastic material suitable for moulding or shaping may be manufactured as follows: Cellulose, e.g., cotton wool—(50 parts) is soaked in a mixture of sulfuric acid, 720, water, 400, and glacial acetic acid, 200 parts for from 12 to 20 hours. The solution is diluted with water, the "fluid-like" cellulose material separated from surplus acid by filtration and decantation, washed, dried and powdered. Five parts of the powdered material are then mixed with glacial acetic acid, 100, acetic anhydride, 100, acetone, 50, carbon tetrachloride, 50, and chemically pure glycerol, 5 parts. The mass thus obtained may be mixed with suitable loading or filling material for moulding into the desired objects.

According to W. Lindsay,[3] plastic masses may be formed by incorporating acetone-soluble acetylcellulose with camphor and either methyl or ethyl alcohols, the proportion of the alcohol being about 1-1.5 times that of the camphor, and 0.5 that of the acetylcellulose. When ethyl alcohol is used, the mixture is preferably heated.

1. F.P. 463156, 1913; abst. J.S.C.I. 1914, **33**, 417; CA. 1914, **8**, 2817.

2. E.P. 23728, 1912; abst. J.S.C.I. 1913, **32**, 1104.

3. U.S.P. 1076215, 1076216, 1913; abst. J.S.C.I. 1913, **32**, 1104; C.A. 1914, **8**, 246, 247. See also C.A. 1913, **7**, 889, 3025.

Knoll & Co.[1] produce acetate plastics by combining alcohol-soluble or acetone-soluble acetylcellulose with high boiling aromatic esters and give the following composition as illustrative of their process: Cellulose is acetylated preferably according to the directions given in German patent 203178, and mixed with 3-10% of *b*-naphthyl benzoate (benzonaphthol), 1-5% of ethyl tartrate and 0.5-5% oleic acid. The mixture is gently warmed for 15-30 minutes, when an entirely clear mixture is said to result. Instead of benzonaphthol may be used methyl, ethyl or propyl benzoates, phthalic acid, anisol or benzyl chloride in about the same amounts as the benzonaphthol employed.

According to the Soc. Anon. Nouvelle l'Oyonnithe[2] extra-supple plastic masses of a basis of nitrocellulose or cellulose accetate are made by incorporating with the usual solvents a very high proportion (50-70% of the weight of cellulose ester) of castor oil, "manol," acetin, etc., with or without pigments or metals, the material being prepared in sheets not exceeding 2 mm. in thickness. Textile fabrics may be combined with these sheets on one or both sides.

Acetylcellulose and celluloid articles, irrespective of their size or configuration, may be cleansed and renovated by the process of A. Pueschel,[3] which comprises immersing the dull or scratched articles in "English sulfuric acid" at the ordinary temperature, followed by washing, drying, and preferably, although not necessarily, steeping in concentrated ethyl alcohol for 15-30 minutes. A final varnishing with one or more coats of camphor-collodion completes the operation.

1. D.R.P. 276013, 1912. See also Knoll & Co., D.R.P. 273706, 1911, same as F.P. 442512; C.A. 1913, **7**, 1288; 1914, **8**, 2948. D.R.P. 274260, 1912. D.R. Anm. K.-36905, 1908. The process of G. Meyer (Aust. P. 55654; D.R. Anm. M.-42978, 1910; abst. Kunst. 1913, **3**, 38), is somewhat similar, the acetone soluble or ethyl acetate soluble acetylcellulose being precipitated by non-solvents and incorporated with camphor substitutes.

2. F.P. 465345, 1913; abst. J.S.C.I. 1914, **33**, 478.

3. E.P. 18105, 1913; abst. J.S.C.I. 1914, **33**, 20; Kunst 1914, **4**, 194; F.P. 461121, 1913; abst. J.S.C.I. 1914, **33**, 196. D.R.P. 270580, 1913; abst. C.A. 1914, **8**, 2252; Kunst. 1914, **4**, 155; D.R. Anm. P.-31300, 1913; abst. Kunst. 1913, **3**, 439; 1914, **4**, 80. Belg. P. 259019; Aust. P. 65040; abst. Kunst. 1914, **4**, 238, 274.

According to another process[1] flexible plastic material may be produced by adding to camphorated nitrocellulose or acetylcellulose large proportions of castor and similar oils, together with such substances as manol and acetin, with mineral compounds and colors. The films produced are used in millinery, and in fibrous form may be made up into washable cravats.

L. Collardon[2] prepares plastic masses from casein, casein-

1. Societe Anonyme Nouvelle l'Oyonnithe, F.P. 465345, 1913; abst. C.A. 1914, 8, 3503.

2. U.S.P. 830493, 1906; L. Collardon (U.S.P. 1105619, 1914; abst. C.A. 1914, 8, 3244) prepares an anti-fouling paint or varnish composed of the condensation products of formaldehyde and phenols and their homologues, which are mixed with cellulose esters of the fatty acid series by means of a solvent or solvent combination which will dissolve both the condensation product and the cellulose ester. With paints a compound of a poisonous nature is added, and in the case of a varnish, a bleaching compound is usually incorporated. Colophony, other resins, and rubber may be added.

In the preparation of a paint of this nature phenol or other suitable phenols is mixed with organic or inorganic compounds of a poisonous nature, such as mercury or arsenic compounds, and to these are added an equal quantity of formaldehyde or para-formaldehyde and the necessary quantiy of water. The resulting mixture is heated in a closed vessel and is well stirred during the heating. After the lapse of a certain time, in the majority of cases two hours, a soft and sticky condensate of resinous nature will be produced. The vessel is then opened and the water removed from the condensate, which is thereafter again heated. After this last drying operation the soft and sticky condensate is mixed with one or more of the cellulose esters, such as cellulose formate, acetate, butyrate, palmitate or other fatty acid ester. This operation is preferably effected in a mixing apparatus which is slightly heated, and the cellulose compound or compounds is or are comminuted to insure the production of a homogeneous mass. A solvent, in which both the condensate and cellulose compounds are soluble, such, for instance, as dichlorethylene, trichlorethylene, dichlorbenzene, acetone, or carbon tetrachlorid, is then added. The product, when reduced to the necessary consistency by the above named solvents can, with the addition of the required pigment, be used as a paint.

If desired jelutong resin or other rubber resin, as well as the so-called semi-resins, which are hydrocarbons obtained from guttapercha, balata and similar trees, or rubber, particularly rubber containing a large amount of resin, guttapercha or balata or rubber-like substances may be added to the carbolic acid or other phenols, as these act as solvents for such resins and rubber or rubber-like substances, altering them to such an extent that they lose their excessive stickiness and acquire other characteristics in the condensation products.

In the case of the manufacture of varnishes according to the present invention carbolic acid or other suitable phenols with the addition of suitable compounds of a poisonous nature would be used in conjunction with formaldehyde or para-formaldehyde together

ates, albumins and albuminous substances by combining them either with acetylcellulose or viscose, the masses being characterized by their hardness, resistance to water, and inferior combustibility to celluloid. The material may be further hardened by acting upon the casein with formaldehyde or hexamethylenetetramine, added either before or during the working-up process. A superficial hardening may also be effected after the working-up. Cellulose esters like the acetate, butyrate, aceto-butyrate, palmitate and phenylacetate, are said to present the property of being soluble in those solvents, which at the same time present a certain capacity for dissolving casein. Owing to this, the patentee claims it is possible to effect the mixing of the various substances with the employment of one solvent, and at the same time the admixture of casein to the cellulose ester and to the solvent causes the cellulose esters to assume a certain hardness and elasticity. If the esters are admixed with the solvent without the incorporation of casein it is necessary to employ heat and pressure in order to obtain a homogeneous mixture. With this process setting is said to take place speedily, which is apparently attributable to the fact that the casein absorbs and neutralizes the solvent.

As substances or solutions suitably adapted as solvents in the present process may be included chloroform, chloral hydrate, pyridine, hydroxylamine, aniline, methylaniline, dimethylaniline, "formic acid ester," "salicylic acid ester."

with bleaching bodies or agents such as sulfurous acid either by itself or in conjunction with other substances, which will produce substantially colorless condensation products. The condensing medium need not be concentrated, weak solutions of from one to ten per cent. being strong enough. As in the case of paints water is removed from the condensate and the latter afterward heated to remove any remaining moisture. The condensate is then mixed with one or more cellulose esters of the fatty acids. The product is then dissolved in carbon tetrachlorid, chlorbenzol, tetrachlorethane, perchlorethylene, pentachlorethane, a solution of hexachlorethane, or mixtures of these or other suitable solvents.

The improved paints and varnishes will be found to be superior to ordinary paints and varnishes as they are absolutely water and acid proof and are not affected by the action of the atmosphere. Further, as the improved paints contain ingredients which are poisonous to barnacles and the like they are especially suitable for painting the submerged parts of vessels.

esters of glycose sugars, lactose, levulose, saccharose, acetochlorhydrose, glycose dibutyrate, tri-, pent- and octa-acetate; saccharose mono-, tetra-, hepta- and octa-acetate, and acid esters such as "sebacine," phosphoric or benzoic acids.

To carry the process into effect, one part of dry cellulose acetate is mixed with an equal quantity of epichlorhydrin and kneaded or worked up in a mixing machine until a tenacious elastic mass is formed. Finely powdered casein is then added until the mass becomes transparent when mixed together. The quantity of casein added depends upon the degree of hardness desired in the finished product. By increasing the quantity of casein added to four times the amount of acetylcellulose taken, the hardness is materially augmented. During mixing it is preferable to keep the mass at a temperature of 40-50°, pressure being simultaneously employed.

In place of casein, other albumens and albuminous substances have proved valuable, especially earth-nut cake, and the cellulose esters may be employed either separately or mixed together, cellulose acetate and cellulose palmitate having proved suitable. The characteristic feature belonging to the solvents should be their ready solubility of casein, albumen and the cellulose ester employed. Cellulose xanthate may also be worked up with the acetated celluloses.

Cellit (cellite, zellith, zellit) is the trade name for a partially hydrated, acetone-soluble cellulose acetate produced by the Farben-fabriken vorm. F. Bayer & Co., and their chemists, A. Eichengruen and T. Becker,[1] and was first supposedly pro-

1. For general articles on Cellit and its applications, see Sci. Amer. 1908, **98**, 370; 1912, **107**, 145. F. Beltzer, Mon. Sci. 1908, **68**, 648; abst. J.S.C.I. 1908, **27**, 1037; Mon. Sci. 1910, (4), **70**, 145; abst. C.A. 1910, **4**, 1238; Chem. Zentr. 1910, **81**, II, 509. L. Clement and C. Riviere, La Rev. de Chim. Ind. 1911, **22**, 215. Caout. and Guttap. 1911, **8**, 5449; abst. C.A. 1911, **5**, 3908. A. Eichengruen, Zts. ang. Chem. 1907, **20**, 922; 1911, **24**, 366. U. S. Daily Consular and Trade Report, Oct. 27, 1908, No. 3315, 13; Jour. Soc. Arts, 1908, **56**, 1009; 1908, **57**, 78. Phot. Dealer, London, 1909, 24; Chem. Ztg. 1908, **32**, 583; Zts. ang. Chem. 1908, **21**, 1729; abst. Chem. Zentr. 1908, **79**, II, 1215; Zts. ang. Chem. 1908, **21**, 1354; Bull. Soc. Chim. 1909, (4), **6**, 74; Zts. ang. Chem. 1911, **24**, 1306; abst. Kunst. 1911, **1**, 452. Oest, Chem. Ztg. 1911, **14**, 59; abst. J.S.C.I. 1911, **30**, 413; C.A. 1911, **5**, 2429. Apoth. Ztg. 1911, **26**, 206; abst. Mercks Report 1911, **20**, 170; Zts. ang. Chem. 1911, **24**, 366; abst. Chem. News, 1911, **103**, 293; 1911, **104**, 203; Jour. Eng.

duced according to their English and French patents of 1901.[1] The method stated is to form a mixture of 100 parts of acetylized cellulose prepared by the action of acetic anhydride and sulfuric acid on cellulose at ordinary temperature, and 50 parts of camphor, the mass being triturated with chloroform or glacial acetic acid. After standing for some hours and gently heating the solid parts dissolve to a more or less transparent liquid. On evaporating the liquid off in any appropriate manner, the "new celluloid-like substance" remains in the shape of a translucid, uncolored, flexible mass, burning slowly, and which can easily be worked by rollers while still hot. Instead of camphor, other bodies may be employed "which by their action impart plasticity[2] to the mixture in the preparation of celluloid, such as *p*-toluene sulphamide, methyl ester of *p*-toluenesulphamic acid, napthalene, etc." When formed into sheets, the films are distinguished by their great stability, and may be kept for a long time without altering.

The next important advancement was in preparing a cellu-

Chem. 1911, **3**, 437. Fabriks Feuerwehr, 1908, **15**, 61. Seifenfabr. 1908, **28**, 946; Chem. Ztg. 1908, **32**, 583; Zts. ang. Chem. 1908, **21**, 1729. Phot. Wochbl. 1908, **19**, 702. Z. Drechsler, 1908, **31**, 375. Am. Apoth. 1908, **29**, 40. C. Hennings, Photg. Jour. 1913, 10. Kunst. 1913, **3**, 298. Kunst. 1911, **1**, 93.

1. U.S.P. 738533, 1903; abst. J.S.C.I. 1903, **22**, 1100. E.P. 26075, 1901; abst. J.S.C.I. 1902, **21**, 1469. F.P. 317008, 1901; abst. J.S.C.I. 1902, **21**, 873.

2. Eichengruen and Becker, U.S.P. 734123, 1903; E.P. 28733, 1904, the process differing from that of Lederer (U.S.P. 654988, 1900) in that a larger quantity of sulfuric acid is employed, and in contradistinction to the acetylcellulose obtained by Lederer, the patentees' ester is soluble in alcohol. The process is carried out as follows, all parts being by weight: 125 parts of hydrocellulose are introduced into a mixture prepared from 500 parts of glacial acetic acid, 500 parts of acetic anhydride and 25 parts of sulfuric acid of 66° Be. The reaction mixture is allowed to stand at the ordinary temperature on stirring it from time to time. After some hours the hydrocellulose is dissolved, and the reaction mass forms a thin liquid solution which can easily be filtered. Subsequently it is poured into water, by which means the product is precipitated in the shape of white flakes, which are filtered off and dissolved in five times its quantity of alcohol. On cooling the resulting solution grows stiff to a mass like gelatin. The acetylized cellulose is a white mass readily soluble in alcohol. Its concentrated alcoholic solution represents in the cold a solid mass like gelatin, which liquifies on heating or on adding alcohol. From the solutions in alcohol, acetone, or glacial acetic acid, the ester is precipitated in the shape of white flakes by the addition of water.

lose acetate which differed from the ester of the older art by its stability against cold alkaline carbonates and ammonia, and by the property of being difficultly attacked by caustic alkalis. In carrying out the process of manufacturing this product, 200 parts of cellulose[1] are introduced into a mixture of 800 parts of acetic anhydride and 20 parts of concentrated sulphuric acid, and the mixture thus obtained diluted with an equal volume of glacial acetic acid. The reaction mass is allowed to stand for twelve to twenty-four hours, the temperature rising the while to 40-45°. It is advisable to keep the temperature at a lower degree by cooling. The clear, nearly colorless thick liquid thus obtained is then poured into water, the acetyl cellulose separating out. Thus prepared it is a whitish voluminous mass. In a dry state it is readily soluble in chloroform, epichlorhydrin, nitrobenzene, and glacial acetic acid, soluble in acetone and pyridine and insoluble in alcohol, ether, ethylacetate, amyl acetate, or glycerol. It is not attacked by cold alkaline carbonates, ammonia, or dilute acids, and by caustic alkalis with difficulty. On evaporating the solutions a colorless and translucid film remains, which is, even in a thickness of half a millimeter, very flexible. The concentrated solutions, especially that in glacial acetic acid, have the characeteristic property that on being poured into a liquid which does not dissolve the acetylized cellulose—such as water, alcohol, or formic aldehyde—they deposit peculiar cylindric precipitates, including a large quantity of the liquid. On drying, the said precipitates shrink to hard oblong bodies. The new acetyl cellulose is decomposed on heating it to about 250°, analysis showing the new product to be a triacetyl derivative.

The glacial acetic acid and especially chloroform used as

1. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, (4), **60**, 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1906, **24**, 686. D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, **75**, II, 625; Jahr. Chem. 1904, 1168; J.C.S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D.R.P. 159524, 1901; abst. Chem. Centr. 1905, **76**, II, 526; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, 984; J.C.S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870. E.P. 21628, 1901; abst. J.S.C.I. 1902, **21**, 870. Aust. P. 31391; It. P. 62042, 1901. See also A. Eichengruen, Aust. Anm. A.-6220, 1910; abst. Kunst. 1912, **2**, 320.

solvents were soon found to be unduly expensive as compared with the fluids used technically in the similarly useful nitrocellulose preparations, but Eichengruen and Becker discovered that in preparing the acetate according to the method described in U.S.P. 790565, 1905, the reaction really occurs in two phases. At first an acetate is produced which is soluble in alcohol, this product being then transformed by the further action of acetic anhydride and sulfuric acid into the triacetyl cellulose insoluble in alcohol. They next succeeded in carrying out the action of acetic anhydride and sulfuric acid on cellulose in such a way that the acetate, soluble in alcohol, is prepared as chief product. For this purpose the process is stopped when the body soluble in alcohol as first produced, begins to be transformed into the triacetyl cellulose insoluble in alcohol.

In carrying out this process practically the following formula may be used, the parts being by weight: A mixture of 80 parts of acetic anhydride, 80 parts of glacial acetic acid, 4 parts of concentrated sulfuric acid, and 20 parts of cellulose (e. g., cotton) is allowed to stand at from 20-25°, with stirring from time to time. After about ten hours the whole mass is transformed into a thick syrup. When the precipitate obtained by diluting a test portion with water contains only a small quantity of unchanged particles of cellulose and is still soluble in hot alcohol, the production of the cellulose acetate is completed. The reaction mass is then mixed with a large quantity of water by stirring, and the precipitate obtained filtered off and pressed. The ester thus obtained is solid and can take various forms, according to the way in which it is prepared. In a wet state it is a whitish voluminous mass, which, when dry, represents yellowish hard lumps. It can also be obtained in transparent sheets and films by evaporation of its solutions. It is soluble in 70% hot alcohol, the alcoholic solution solidifying to a gelatinous mass on cooling. By the addition of much water to the alcoholic solution the ester is precipitated in fine light flakes.

By treating this form of acetylhydrocellulose with camphor and a mixture of alcohol and ethyl acetate(the most efficient of the inexpensive solvent combinations for this ester)

as described above, a plastic product may be formed, the material possessing the three valuable requisites of uninflammability, plasticity, and dissolution in comparatively inexpensive solvent mixtures.[1] While bodies of this nature can never

1. In the U. S. Daily Consular and Trade Rep., No. 3244, Aug. 4, 1908, p. 12, and No. 3315, Oct. 27, 1908, p. 12, reprinted Jour. Roy. Soc. Arts, 1908, 56, 1009; 1908, 57, 78; Photographic Dealer (Lond.), 1909, Jan., p. 24, is given the following data supplied by the inventors of Cellit and communicated to the U. S. Consul at Chemnitz:

"It is easily soluble in such solvents as alcohol or acetic ether, which do not seriously affect the health of workmen; and, what is more important, it combines with camphor exactly as does guncotton, yielding plastic masses quite similar to ordinary celluloid. Camphor can be replaced by other organic substances, and the resultant products range from hard and tough to soft, leather-like, even rubber-like compositions. All of these varied forms of cellit are perfectly transparent, totally unaffected by water, free from brittleness, and, above all, not readily combustible. Some varieties do not burn at all. Others burn in a flame, but combustion ceases when the flame is removed.

"The different properties of cellit are characteristic of glass, gelatin, celluloid, leather, and rubber, and it is capable of replacing each of these materials for divers purposes. Probably new technical applications will soon arise, as we have lacked hitherto a substance at once transparent as glass and pliable as a woven fabric.

"It would seem to lend itself admirably for decorative effects, as it can be molded like crystal or receive the delicate imprint of the finest designs. The sheets of cellit are prepared in all degrees of hardness for the purpose of receiving impressions. The results sometimes resemble enamel, again fine leather, or entirely novel effects are evolved. Especially interesting are the specimens of patent leather and of linoleum coated with cellit. The designs of the linoleum are not printed on the surface of the tissue, but are part of the transparent cellit coating with greatly enhanced effect.

"Cellit insulation for electric wires combines the advantages over the present materials of cheapness and more attractive appearance, while occupying less space.

"A distinct field exists for cellit in preparing waterproof, airtight containers for perfumery, bonbons, etc.; in meeting many needs of the bookbinder and of the surgeon; in the manufacture of toys, fans, and various articles of domestic use where resistance to water and pliability are the chief requirements.

"To what extent cellit can replace celluloid is not yet definitely ascertained. Certain technical difficulties have recently been overcome in blowing articles of the new substance. Such hollow objects as balls, dolls' heads, and the like are now as easily prepared as from celluloid.

"The latest application is among the most important. It is the use of cellit films for the cinematograph. Its manifest superiority over celluloid for this purpose results from its non-combustibility.

"A cellit film exposed for ten minutes to the concentrated light of an arc lamp does not exhibit the slightest alteration. A celluloid

hope to successfully compete with celluloid for general tech-

film, under the same conditions, bursts into flame after the lapse of only three seconds. The cinematograph has now entered so extensively into the category of popular entertainments that a film material will be most welcome which will obviate the serious danger thus far attendant upon the employment of the current mechanism and already productive of several tragic catastrophies.

"The acetates first obtained during recent years yielded in combination with camphor more or less brittle substances. Their only satisfactory solvents were chloroform and acetylene tetrachloride. The narcotic action of the first solvent and the poisonous nature of the latter rendered their use most objectionable. These disadvantages, in addition to the brittleness, effectually prevented any practical use of the earlier forms of acetylcellulose for use in the cinematograph, although numerous experiments in this direction were carried on for a long period.

"The newly discovered modification, in its camphor derivative termed cellit, possesses fortunately the desired properties, missing its homologues. It is the reverse of brittle, resembling leather, and it is readily soluble in the comparatively cheap mixture of alcohol and acetic ether (ethyl acetate).

"With these two all-important properties to start with, much study and experiments were required before a cellit was secured meeting all the many demands made upon cinematograph films. Celluloid (the combination of camphor and guncotton) is characterized by its hardness, springiness, and tenacity. A multitude of difficulties in this connection were gradually overcome, until cellit films were finally prepared, free from liability to tear or stretch or crumple. In the cinematographic apparatus there is now no scratching of the surface no tearing, no distortion on the part of cellit films when swiftly passed through the mechanism.

"The various other technical difficulties in connection with the application and fixation of the sensitive emulsion, the securing of uniform transparency, etc., have all been successfully met, so that the new films are scarcely to be distinguished from celluloid preparations so far as luster, tenacity, evenness, transparency, etc., are concerned.

"In one respect, however, there is the most striking and important difference, and this is inflammability. When celluloid is brought near a source of heat it instantly takes fire, burning with a large, crackling flame, which spreads so rapidly that all possibility of extinction is practically precluded. On the contrary, when a burning match is applied to a cellit film, it does not take fire at once, but only after an interval. Then a slow combustion, accompanied by a small flame, begins, and is gradually propagated through the mass, very much as in the case of a sheet of india-rubber. A cellit film behaves often as a stick of sealing-wax. It tends to melt, and while the molten substance falls down in drops the flame is often extinguished.

"While cellit films in contact with a flame exhibit such a measure of slow combustibility, they are entirely incombustible in the cinematographic apparatus. Even when exposed to the concentrated rays of the most powerful arc lamp, there is no sign of combustion. When the exposure is prolonged changes become evident in the film; the layer of emulsion is loosened, blisters appear, there is a general shrinkage, and finally fusion begins along the lines of the photo-

nical use owing to the present great discrepancy in cost of acetic acid, acetic anhydride and acetyl chloride as compared with nitric acid, its present field appears to be in the preparation of uninflammable photographic films, for which purpose it is being produced in large quantities at the present time. Perhaps at the present time the largest individual user of uninflammable cinematographic films in Europe is the firm of Pathe Frères, of Paris, and it is understood that this firm is at present using a cellulose acetate plastic film, produced by this general method.

Eichengruen has apparently determined[1] that certain types of cellulose acetate, notably those which are soluble in acetone, are soluble, on heating, in mixtures of liquids, e.g.,

graphic picture. The action ceases with this result, even if the exposure be maintained for an hour.

"The behavior of a celluloid film under such conditions is all too well known. It is impossible to adjust it in the apparatus without full protection from the source of light. If exposed for a second it begins to smoke, and within four seconds, at the utmost, it bursts into flame.

"This unfortunate property has rendered the cinematograph such a source of danger, when, through any accidental interruption of the rapid movement of the celluloid films before the powerful sources of light, or even through the tearing of a film, instantaneous combustion ensues.

"Preventive measures designed to lessen the danger have been taken in various countries by the police authorities and are of the most manifold variety. There are requirements for the inclosure of the apparatus in a fireproof cell during an exhibition, for its operation in a room covered with asbestos, outside of an exhibition hall, for the use of asbestos clothing by the operators, for the entire absence of flame-giving lights, etc.

"Numerous attempts have been made to replace celluloid as a material for films. Gelatin has been tried in a multitude of forms. Its lack of strength and its tendency to swell up in developing baths have prevented any practical application for the purpose. Even when inclosed between exceedingly thin sheets of celluloid it fails to withstand the effects of the bath. Other albuminous bodies lack in plasticity and transparency."

1. U.S.P. 1015156, 1912; abst. Mon. Sci. 1912, **77**, 163. E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1005; Chem. Tech. Rep. 1911, **35**, 340. E.P. 18076, 1910, being First Add. to E.P. 1441, 1910; abst. J.S.C.I. 1910, **29**, 1199. F.P. 412797, 1910; abst. Rev. Chim. Ind. 1910, **21**, 257; J.S.C.I. 1910, **29**, 1199. First Add. 12388, Mar. 19, 1910, to F.P. 412797; abst. J.S.C.I. 1910, **29**, 1199. D.R.P. 238348, 1909; abst. C.A. 1912, **6**, 1672; Chem. Zentr. 1911, **82**, 1085; Chem. Ind. 1911, **34**, 637; Chem. Tech. Rep. 1911, **35**, 520. Aust. P. 47899; Swiss P. 52115; abst. Kunst. 1912, **2**, 99. Can. P. 129265, 1910.

methyl alsohol and benzene, neither of which have any solvent action alone. On cooling these solutions, the ester may either remain in solution or separate out in the form of long felted filaments. This tendency to separation may be prevented by adding to the solution any of the ordinary solvents of cellulose acetate, in which it is soluble in the cold, e.g., glacial acetic acid, acetone, etc., in which case the solution remains liquid or becomes syrupy on cooling; or else, there may be added a substance having a solvent action analogous to that of camphor on nitrocellulose, in which case the solution sets to a continuous mass on cooling. Suitable bodies are methylacetanilide, ethyl toluenesulphonate, trichloraniline, etc. If a very concentrated mass is desired, the cellulose acetate may be dissolved in alcohol and benzene, freed from impurities by filtration and allowed to deposit by cooling; the liquid is then poured off and the precipitated cellulose acetate worked up with a camphor substitute. One of the numerous examples of the process is as follows: 1 k. of cellulose acetate is dissolved in 2 k. of methyl alcohol and 1 k. of toluene at 80°; 150 gm. of methylacetanilide are added to the solution and 100 gm. of epichlorhydrin. The liquid is filtered hot, and on cooling sets to a solid mass, which may be sliced, molded or forced through orifices. The spreading of fine films or coatings of cellulose acetate on materials or fabrics of porous or uneven surface is difficult, because the coating tends to sink into or take the form of the body-material. According to Eichengruen a thin film of a solution of the acetate is spread on a support having an even, close or polished surface, to which the film, when fully dried, will not adhere. The film, before it is completely dry, is then pressed in contact with the body-material to be coated, and drying is completed. The film then peels off the temporary support and adheres firmly to the body-material, while its surface presents an exact reproduction of the surface of the support. Suitable supports are made of metal foil, metallized paper, rubber, waxed cloth, varnished leather, etc. The body-material may be previously moistened with a solvent of the acetate in order to promote adhesion of the film.

The manufacturers recommend the following as satis-

factory solutions of Cellit (also called Cellit L.) for films, lacquers or general use.

18 parts Cellit L.
20 " Acetone
13 " Denatured alcohol
49 " Ethyl acetate.

or

20 parts Cellit L
16 " Denatured alcohol
64 " Acetone.

or

20 parts Cellit L
16 " Denatured alcohol
64 " Ethyl acetate.

or

20 parts Cellit L
80 " Acetone.

Commercial Cellit originally contained camphor as a component. As at present produced, it is a white, amorphous, light, soft powder, insoluble in water, insoluble in cold ethyl alcohol, but plastic in it when heated to 100°; soluble in cold aniline, lactic acid, phenol and 99% acetone; insoluble in cold chloroform, but plastic when the solution is warmed; soluble in cold chloroform upon the addition of 10% alcohol; heated with glycerol to 125° it becomes plastic. Cellit has been claimed by the inventor[1] as a "definite" acetate. It is possible to make a thin sheet suitable for cinematographic films, but 0.25 mm. is the maximum thickness for satisfactory commercial work, for the reason that the concentrated solutions such as required in the formation of thicker sheets, dry from the outside and enclose solvent which is removable entirely only with great difficulty. Leuchter[2] has called attention to the application of Cellit solutions for preserving herbarium specimens, and Goldman for the protection of the hands by thin Cellit coatings.

1. Oesterr. Chem. Ztg. 1911, **14**, 59; abst. J.S.C.I. 1911, **30**, 413; C.A. 1911, **5**, 2429. See A. Eichengruen, Aust. P. 55514; abst. Kunst. 1913, **8**, 38.
2. Chem. Ztg. 1910, **34**, 1137.

Cellon, Sicoid. A. Eichengruen [1] has described cellulose acetates which gelatinize upon cooling from non-solvents, and which are especially useful on this account for the preparation of plastic aggregates, sheets or films. According to this process, acetylcelluloses soluble in acetone or ethyl acetate, also insoluble both in alcohol and in benzene separately, and permanently insoluble in the cold in a mixture of the two, will readily dissolve in a mixture of alcohol and benzene upon the application of heat. A clear solution is obtained by heating to the boiling point of the solvents, which assumes a milky appearance, and from which upon cooling the acetylcellulose quantitatively separates in the form of an amorphous precipitate. If the ester be now separated from excess of solvent and mixed with camphor or camphor substitutes, in order to impart softness and plasticity, and the mass be again heated until homogeneous, a final product results capable of being kneaded, cut, pressed or moulded. The molten mass may also be caused to issue under pressure through various shaped openings to form tubes, threads or bars.

The process is illustrated by the following two examples: 2 k. of acetylcellulose soluble in ethyl acetate are mixed with 20 k. each of alcohol and benzene. The mixture is slowly heated on the water bath with constant stirring, and maintained at a temperature of about 60° for some time, and finally heated to the boiling point. The acetylcellulose dissolves almost instantly, and on cooling precipitates as a soft layer adhering to the sides of the vessel. The excess of solvent is decanted, to the remainder is added 600 gms. camphor and 400 gms. acetochlorhydrin, and the mass heated to 50°. The clear solution thus obtained solidifies upon cooling to a solid

1. U.S.P. 1015156, 1912; abst. Mon. Sci. 1912, 77, 163. E.P. 1441, 1910; abst. J.S.C.I. 1910, 29, 1005; Chem. Tech. Rep. 1911, 35, 340. E.P. 18076, 1910; First Ad. to E.P. 1441, 1910; abst. J.S.C.I. 1910, 29, 1199. F.P. 412797, 1910; abst. J.S.C.I. 1910, 29, 1005; Rev. Chim. Ind. 1910, 21, 257. First Add. 12388, dated Mar. 19, 1910, to F.P. 412797; abst. J.S.C.I. 1910, 29, 1199. D.R.P. 238348, 1909; abst. Chem. Ind. 1911, 34, 637; Chem. Tech. Rep. 1911, 35, 520; C.A. 1912, 6, 1672; Chem. Zentr. 1911, 82, 1085. Aust. P. 47899. Swiss P. 52115; abst. Kunst. 1912, 2, 99. Can. P. 129265, 1910. For article on "Cellon," see Zts. ang. Chem. 1911, 366; Jour. Ind. Eng. Chem. 1911, 3, 437.

compact mass, which can be cut, stamped, rolled or otherwise mechanically treated. Or, 2 k. acetone-soluble acetylcellulose are mixed with 500 gms. of mannol and 250 gms. of creosote, 6 k. methyl alcohol and 4 k. toluene added, and heated to boiling temperature, stirred, and the heat continued until a clear, transparent solution results. The mass cools to a workable, semi-solid block.

Working the above processes, the Rheinisch-Westfalische Sprengstoff Akt-Ges. of Cologne have placed upon the market a cellulose acetate under the name Cellon, and the Societe Industrielle de Celluloid de Paris are manufacturing in France the identical material under the trade name Sicoid.

A. Rost [1] in an illustrated article has detailed the advantages claimed for Cellon, and pointed out its applications for windows for automobiles and air-ships, coating material for the webs of balloons, as a lacquer for the protection of wood and metal, and for filling the interstices of textiles in the formation of waterproofed fabrics and imitation leather.[2]

H. Reeser [3] has also observed that when acetylcellulose, of the type which is soluble in acetone or ethyl acetate, is heated with a mixture of equal parts of benzene and alcohol, it dissolves near the boiling temperature, but separates again on cooling. If the liquid is poured off from the deposit and camphor or a camphor substitute be added to the latter, the mixture again becomes fluid on heating, and the product, when cold, forms a plastic solid having the properties of celluloid. For example, 2 k. of acetylcellulose of the type specified are

1. Kunst. 1913, **3**, 150; abst. C.A. 1913, **7**, 2113. Apyroid, according to Kunst. 1913, **3**, 437, is the name applied to a commercial cellulose acetate product.

2. A. Eichengruen, Oesterr. Chem. Ztg. 1911, **14**, 59; abst. J.S.C.I. 1911, **30**, 413; C.A. 1911, **5**, 2429; Zts. ang. Chem. 1911, **24**, No. 8.

U. S. Daily Consular and Trade Report, Apr. 20, 1911, p. 461. See also Phot. Mitt. 1911, 125. Eders. Jahr. 1911, 528. For "Substitute for Glass," being description of the uses of Cellit and Cellon, see v. Unruh, Kunst. 1913, **3**, 455.

3. Belg. P. 216668. E.P. 12976, 1909; no patent granted; abst. J.S.C.I. 1910, **19**, 147. F.P. 411126, 1909; abst. J.S.C.I. 1910, **29**, 875; Mon. Sci. 1912, **77**, 8. Aust. P. 9533, 1909, Dec. 20, 1909; June 2, 1909. Hung. Anm. R-2398, Dec. 23, 1909. Port. P. 7102, Dec. 12, 1909.

mixed with 20 k. each of alcohol and benzene, the mixture is heated for some time at 60°, and then to boiling until the acetylcellulose is dissolved. After cooling, the solvent is poured off from the mass which separates, 600 gm. of camphor and 400 gm. of acetochlorhydrin are added, and the whole is again heated at 50°, in order to produce a transparent fluid which sets on cooling. If desired, the camphor may be added to the original acetylcellulose and the whole heated with the solvent until dissolved. Homologues of alcohol and benzene respectively may be used.

Sericose is a partially hydrated cellulose acetate, in which the process of hydration has been carried beyond the stage of complete solubility in absolute acetone and plasticity in warm chloroform, to the stage of solubility in ethyl alcohol and in dilute acetic acid. As hydration increases, the final product continues to become softer to the feel. Sericose, therefore, is a soft, white, voluminous powder, with but little tensile strength for film formation, readily soluble in weak acetic acid solutions, from which the hydrated acetate upon evaporation, either with or without a subsequent fixation by means of steam, possesses the property of adhering to textiles, and in doing so to firmly bind into the interstices of the textile fiber various pigments, usually of a white color. Previous to the introduction of partially hydrated cellulose acetate, such bodies as gum arabic, British gum, tragacanth, starch, flour and albumen were used by calico printers for thickening the various colors, but they were all open to various objections, the main one being their proneness to fermentation and other decomposition, so that the solutions when made up had to be used within a short time. In the printing of pigment colors, albumen is used both as a thickening agent and a fixative, and is perhaps the most objectionable of the above named materials on account of its rapid decomposition.

Hydrated cellulose acetates possess the property of permanency in solution as an advantage over the various proteid and carbohydrate thickening agents, and is insoluble under ordinary conditions. In printing with Sericose and Sericose L, from 75-120 parts are dissolved in 1500 parts of acetic

acid of about 40% strength, which is best done by weighing out the required amount of acetic acid and sprinkling it over the hydrated acetate with vigorous stirring. After 12-24 hours standing, or a shorter time if gently warmed, the solution is ready for use. Into this solution may be stirred various amounts of blanc fixe, zinc oxide or zinc white, together with more acetic acid, the patentees advising the following:

200-400 parts blanc fixe (75% paste).
100 parts 80% acetic acid.
500-750 parts Sericose L. solution, prepared as above.

In the printing of pigment colors, the following formula is stated to give desirable results:

40 gms. zinc white,
4 gms. acetylcellulose,
56 gms. alcohol,
20 gms. glycerin,
10 gms. acetone.

After printing, the goods are quickly passed through the Mather-Platt steamer, to remove the acetic acid and to dry the textile.[1] This ester is said to give prints of great fastness to soap, brilliant in shade, the feel of the fabric is but slightly affected, and a much shorter period of steaming suffices than for albumen.

To produce damask effects on table cloths and other textiles, and to produce polka dots, stripes and patterns, hydrated cellulose acetates are being used in increasing quantities. Goods printed with hydrated cellulose acetate may afterwards be slop-padded with direct or substantive colors, with basic and mordant colors, and with aniline black, which may afterwards be discharged or resisted. For basic dyes, either 40% acetic acid solutions, or alcoholic solutions may be used, and added directly to the hydrated acetycellulose mixture, thus admitting of the production of fancy effects in color printing.

1. The amount of acetic acid (i. e., the accuracy of the concentration) in the print colour has great influence on its printing properties and on the fastness of the effects. If the acetic acid is not sufficiently concentrated or if the blanc-fixe paste is not purified, the print color will adhere to the engravings. Of course the fastness and intensity of the effects also depend upon the amount of Sericose employed, and its degree of hydration.

A little tannin in acetic acid may also be used to assist in the fixation of the colors.

In the fixation of metallic colors, pigments and bronzes, less experimentation has been done with the cellulose acetates.[1] A sealed communication opened by the Soc. Ind. de Mulhouse in Mar. 1913[2] gives a formula for printing with metallic powders consisting of Sericose L, phenol, formalin and sodium acetate, the metallic powder being added after heating the liquid on the water bath. The goods are dried and steamed in the usual way. A mixture of phenol and 40% formaldehyde was found to give sufficiently viscous solutions, which are easily printed. The solvents have no action on the metallic powders examined, but dissolve Sericose in the cold. This thickener, however, does not prevent the metallic powders suspended in it from spoiling the design. This disadvantage disappears when the phenol and formaldehyde is condensed in the presence of a small amount of sodium acetate or ammonium acetate. The condensation takes place during the drying and steaming of the fiber, and aids the Sericose in fixing the metallic powder. Less satisfactory results were obtained when useing a Bakelite which is commercial under the name of Metakalin (Bayer & Co.). On steaming the excess of phenol and formaldehyde is driven off. The following thickener gives satisfactory results:

Sericose, 150-200 grms.;
Phenol, 450-500 grms.;
Formaldehyde, 40%, 500 grms.;
Sodium acetate crystals, 50 grms.

The mixture is heated for several hours after dissolving the Sericose, after which the required amount of metallic powder is added. The material is dried, steamed by passing for several minutes through a rapid ager, washed, soaped, rinsed and dried.[3] The report states that remarkably clear prints are obtained.

1. Farbenfabriken vorm. E. Bayer & Co. F.P. 341007, 1904; abst. J.S.C.I. 1904, **23**, 864.

2. J. Heilman, H. Wagner and M. Battegay, Reports Soc. Ind. de Mulhouse Mar. 1913, **83**, 43; sealed note No. 2213, Nov. 26, 1912; abst. Jour. Soc. Dyers Col. 1913, **29**, 196.

3. J. Stephan. Sealed note No. 1287, Sept. 7, 1901. Report

In printing with metals it is evident that acetic acid solutions of acetylcellulose are not applicable, since acetic acid readily attacks the majority of metallic powders. For this work, ethyl alcohol is the usual medium in which the acetated cellulose is dissolved, the following formula being satisfactory:

15 parts acetated cellulose,
12 parts alcohol,
10 parts phenol,
20 parts formaldehyde.

It is necessary that the metals be very finely divided, and free from oil or grease. In producing "mat" or "damask" effects with white pigments no dyestuff is required, while in obtaining the so-called "moire" effects, the steamed and acetylcellulose coated cloth is afterwards lightly dyed over. If the cloth after printing is padded with an aniline black liquor, before ageing, reserves are printed with sodium acetate as the active agent for whites or colored discharges, the result being that after development by ageing, the acetated cellulose pattern stands up as a grey. Or the acetated cellulose may be padded over a chrome mordant and subsequently dyed and discharged by means of oxidation with sodium chlorate.[1] The printing of gold and bronze on very thin silk is in the experimental stage, and its value is still in doubt.

Commercial Sericose L. examined by the author was a white, friable powder, soft to the touch, insoluble in water,

thereon by M. Battegay, Bull. Soc. Mulhouse, 1913, **83**, 56; abst. J.S.C.I. 1913, **32**, 427. The metallic powder is printed along with formaldehyde and ammonia and a thickening which consists of a solution of glue and resorcinol. The material is then dried and steamed for an hour under pressure. The process is based on an observation of the author that a solution of glue or gelatin can be kept fluid by the addition of a soluble phenol. The report refers to sealed note No. 2213 of Nov. 26, 1912, J. Heilmann & Co., H. Wagner, and M. Battegay, in which it is suggested to print metallic powders along with a mixture of "Sericose" (acetylcellulose), phenol, and formaldehyde together with a little sodium acetate or ammonia. In this case fixation is due to the condensation of the formaldehyde and phenol to form a synthetic resin. It seems probable that in the process of sealed note 1287, fixation is to some extent due to the condensation of the formaldehyde with the resorcinol as well as with the gelatin.

1. Text Col. 1904, **26**, 375; 1913, **35**, 61.

and in 99% acetone, but plastic in the latter, especially upon slight warming. Absorbs a large bulk of alcohol-free chloroform, in which it does not become plastic. That is, it has been hydrated beyond the stage of plasticity in hot chloroform, which is the stage best for film formation. A chloroformic suspension of Sericose becomes plastic upon the addition of a small amount of ethyl alcohol. Soluble in acetone carrying a small amount of water, but not to a clear solution. Substantially soluble in 93% acetone.

Boroid and **Cellolite** are commercial names for cellulose acetate products. Under the name of Boroid, Ltd., a company was recently formed in England for the manufacture of incombustible photographic films and artificial silk. The processes are stated to have been developed by Benno Borzykowski. Cellolite, the name applied to the products produced under the cellulose acetate patents of Walters, is understood to have united with the Boroid Co. as controlled by the Photochemie G.m.b.H. in Berlin. Argonite is stated to be similar to Boroid. Apyroid [1] is the name of a cellulose acetate product, a company having been organized in Berlin, Ger., for the manufacture of this celluloid-like material. Cellonit is the name reserved for the acetylated cellulose products of Dreyfus & Co., of Basel, Switzerland. Cellone [2] is a similar product.

Acetate Lacquers.[3] In distinction from pyroxylin lacquers and bronzing fluids, cellulose acetate solutions are relatively uninflammable, due to the slow-burning qualities of the acetic ester, and also to tetrachlorethane, a cellulose acetate solvent of great value in fluid acetate solutions. Not hydrated or normal cellulose acetate is best dissolved by chloroform, which, although uninflammable, is too expensive for commercial use, so that at the present time no chloroform-cellulose acetate lacquers are on the market. By progressive hydration from a chloroform-soluble cellulose acetate,

1. Kunst. 1913, **3**, 437.

2. According to the Journal of Commerce and Commercial Bulletin, N. Y. City, of Aug. 10, 1914, The American Cellone Company has been incorporated in New York State.

3. For general article see Kunst. 1912, **2**, 239; L. Clement, Mat. grass. 1911, 2423; Kunst. 1912, **2**, 32.

solubility in the latter solvent decreases while the proportion of ester soluble in substantially pure acetone increases. It is these acetone-soluble acetates, or an acetate which has not been hydrated quite so far as to be acetone-soluble but which is readily dissolved by tetrachlorethane and either methyl or ethyl alcohols, which produce technically the most useful lacquers. Heat is usually required to properly dissolve the acetated cellulose, and often the tetrachlorethane lacquers gelatinize upon cooling and require to be re-warmed before use.

These lacquers are preferably composed of a solvent (tetrachlorethane and alcohol, acetone, ethyl acetate) and non-solvent portion, the latter being a volatile fluid added either to impart some desirable property, or more often to reduce the cost. The two classes of non-solvents used are the petroleum benzines and the commercial benzols and toluols, both classes being non-hygroscopic, water-insoluble colorless liquids, readily miscible without turbidity with the cellulose acetate solvents. The petroleum benzines although the less expensive are seldom used, the 90% and 100% benzols being preferable on account of their property of imparting luster and also because they may be added in larger amounts to an acetate lacquer without precipitation of the ester. Therefore, although the first cost of the benzols is higher than the petroleum benzines, taking into consideration the larger amount of the former which may be used for thinning or diluting purposes, the discrepancy in price is not so noticeable. The 100% benzol is probably preferable as containing less of the higher-boiling, cellulose acetate-nonsolvents toluene and xylene, and also on account of its water-white appearance, although it has a tendency to crystallize in cold weather. By a judicious manipulation of tetrachlorethane, alcohol and acetone, or the purified light acetone oils (containing methyl-, ethyl, and di-ethyl ketones) it is possible to introduce into a cellulose acetate lacquer formula 60%-65% benzol without a deterioration of its desirable qualities of free-flowing, clearness, luster and quick-drying.

The general method of preparation of these lacquers is

to first dry the cellulose acetate, after which it is dissolved in the solvent portion of the lacquer formula, the composition of the solvent portion depending upon the degree of hydrolysis of the acetate used and the use to which the finished preparation is intended to be applied. After the acetate has been thoroughly dissolved by from 75%-80% of the solvent portion, the remainder of the solvent is mixed with the non-solvent. and this fluid incorporated slowly with the dissolved cellulose ester with (preferably) continual agitation. After entire solution, the lacquer is either clarified from imperfectly dissolved fibers and extraneous impurities by long settling in glass-lined or enameled vertical tanks, or more quickly by gravity or pressure filtration through paper, felt, mole-skin, dry sand, asbestos or flannel. In artificial filament or continuous film formation, it is essential that the clarification be as complete as possible. If it is desired to prepare a mixed acetate-resin lacquer the resin is first dissolved in tetrachlorethane and filtered. This fluid is an excellent solvent for dammar, sandarac, elemi, shellac, kauri copal and the softer ambers. The filtered resin solution is then incorporated with the neutral ester in solution in the proportions desired. Solution of the resins is aided by the application of a gentle heat and agitation. It is not considered good practice to attempt to dissolve the resin and acetate at the same time in the same solution. Cellulose acetate is of value both in dip and brush lacquers. The former class of solutions is intended for application where the article to be coated is immersed in the lacquer, these solutions, therefore, being used more for protective than ornamental purposes. Like the corresponding nitrocellulose solutions the total solids seldom exceed 4%, so that when an article is dipped in a solution of this nature and the volatile portion evaporated, the solid residue will be in amount just sufficient to properly protect the surface from atmospheric influences, and yet insufficient to be visible. The ideal dip lacquer—irrespective of its composition—is one which combines greatest tenacity and maximum covering power with the least residue deposited. On highly polished metallic surfaces they should deposit indistinguishable but

water-repellant pellicles which in no way alters the luster or appearance of the surface to which it is applied. Unlike the pyroxylin dip lacquers, the specific gravity is usually greater than one, due to the presence of the relatively heavy tetrachlorethane, whereas there is no pyroxylin solvent in commercial use with a specific gravity greater than 1.0. The viscosity or flow is no criterion of the percentage of acetate contained therein or the amount of acetic acid which is in combination with cellulose to form the acetate. In this respect the acetic esters resemble the cellulose nitrates.

Bronzing liquids are really dip lacquers due to the admixture of metals before use. Where the statuary or other piece to be coated has a peculiar or intricate configuration, dip lacquers may be applied by brushing, but such instances are comparatively rare.

The brush lacquers, which are intended primarily for adornment, have a much higher percentage of total solids than the dip lacquers, often containing as high as 4 lb. to the gallon of combined resin and cellulose ester. It is a peculiar fact that resins may be added to acetate solutions in large amounts with but little increase in viscosity, and hence the "flowable" qualities of the lacquer upon which its covering power mainly depends, is but little affected. Material of a porous nature as wood would require an indefinite number of coats of a dip lacquer to effectually fill the pores. Hence for this class of work solutions with large percentages of solid residue upon evaporation are most desired.

Waste cellulose acetate (n.i.) film is useful for brush and dip lacquer manufacture and can be obtained in the United States with the gelatin attached for from three to eight cents per pound. By dissolving off the gelatin with steam, weak alkali or peptonizing agents as pepsin, the silver contained in the gelatin may be recovered by evaporating the aqueous solution to dryness and igniting, while the acetate film substantially free from gelatin and silver, may be used directly for acetate lacquer manufacture. Films which have had the gelatin removed by processes in which water has entered are often stained. In order to produce colorless and transparent

solutions from such acetate film stock it may be dissolved in a light boiling solvent (acetone) and precipitated with a high-boiling non-solvent (xylol), the acetone being afterwards separated from the xylol by means of a water-bath fractionation. Or, the acetone solution of cellulose acetate may be bleached by precipitation in an aqueous bath which contains sufficient hydrogen dioxide to obtain the result desired. In either instance the precipitated flocculent acetate after drying is in condition for profitable re-use.

While the acetate lacquers are relatively uninflammable, being less so with increase of tetrachlorethane, chloroform or pentachlorethane, and more so with increase of alcohol, acetone, ethyl acetate or the commercial benzols, the inflammability may be still further reduced by the introduction of such non-aqueous silicic esters as methyl, ethyl, propyl, butyl or amyl silicates,[1] molybdenum salts,[2] and the potassium, sodium or ammonium metavanadates, paratungstates and metantimonates.

Irrespective of the ester or resin contained in the formula, the relative solubility of the solvent and non-solvent fluids comprising the formulas must continually be borne in mind, and they should be so adjusted that at no point in the evaporative process from the moment of application until a solid film is produced does the non-solvent constituent or constituents predominate to a point of precipitation of the ester or resin contained in the lacquer. It is not sufficient that the finished formula shall contain no excess of non-solvent, for a lacquer containing low-boiling solvent (say acetone) and high-boiling non-solvent (as xylol), when drying after application will lose the acetone faster than the more slowly evaporating xylol, so that as the evaporative process proceeds the increment of non-solvent to solvent continually increases, and that ratio may increase to a point where the resin or ester is thrown out of solution in a form devoid of elasticity, ten-

1. U.S.P. 794581, 1905. For resume of cellulose acetate lacquers see L. Clement and C. Riviere, Caut. et Gutta P., 1912, 8, 5615; abst. C. A. 1912, 6, 806. Also Anon. Papier Ztg; reproduced Chem. Tech. Fabrikant 1912, 9, 553; abst. Kunst. 1912, 2, 239.

2. E.P. 22085, 1909.

acity or strength. Incipient precipitation of this nature is usually observable by the film becoming granular, opalescent and often milky in appearance. In a properly balanced formula the ratio between the solvent and non-solvent fluid portion is so adjusted that the equilibrium is not disturbed, and the liquid of slowest evaporative power in each instance is a solvent of the solids. This can readily be adjusted with acetate lacquers by employing tetrachlorethane.

Cellulose acetate is capable of standing a higher heat than the cellulose nitrates without detriment or decomposition, which is an important point of superiority of the acetates for electric wire insulation. Therefore in lacquers intended for coating surfaces exposed to heat, such as steam pipes, registers, radiators, etc., acetate lacquers high in tetrachlorethane make desirable preparations. Boiled linseed oil which is used with pyroxylin may be added, a suitable formula being:

	Parts by Weight.
Cellulose acetate	8
Copal	6
Boiled linseed oil	12
Tetrachlorethane	35
Acetone	22
Light acetone oil	12
Benzol 100%	30

The cellulose acetate is dissolved in a portion of the tetrachlorethane and all of the acetone, and the resin in the balance of the tetrachlorethane and the acetone oil. After filtration of the resin solution the two are united, benzol added, and finally the oil incorporated by stirring.

A suitable dip lacquer may consist of:

	Parts by Weight.
Cellulose acetate	7
Ethyl acetate	12
Tetrachlorethane	22
Denatured ethyl alcohol	4
Acetone	12
Benzol 90% or 100%	52

The solvents are mixed together, the cellulose acetate

dissolved therein, the benzol added slowly, and the finished solution clarified by subsidence or filtration before use.

In a formula similar to the above, and in which tetrachlorethane comprises the major portion of the solvent part, the lacquer shows the physical advantages of the tetrachlorethane in that it is non-hydrous, not hygroscopic, the boiling point is high, and yet the vapor tension of the tetrachlorethane is sufficient to cause rapid evaporation. The fact that the tetrachlorethane is insoluble in water allows its use in lacquers in a moist atmosphere without observable detriment. The volatility and evaporation of the lacquer may be readily modified and its speed of drying lessened or increased by a partial replacement of tetrachlorethane (b. pt. 147°) by such volatile solvents as dichlorethylene (b. pt. 85°) or pentachlorethane (b. pt. 159°C). These two liquids, especially upon the addition of alcohol, produce solvents for a wide range of cellulose acetates.

The pliability and elasticity of the lacquer film may be enhanced by the use of varying amounts of camphor substitutes, such as triphenyl phosphate, tricresyl phosphate, the acetins, resorcinol diacetate, pyrogallol triacetate and similarly acting bodies.

G. Koller[1] prepares a lacquer composition by treating acetylcellulose with phenol, and trichlorethylene or perchlorethylene.

In a brush lacquer, the resin selected will depend upon the nature of the material to be coated and the use to which the coated article is to be placed. For photographs, documents and general paper protection, dammar is excellent and will dissolve readily in the usual solvents of an acetate lacquer formula. Kauri copal is best for a floor lacquer in combination with cellulose acetate, such a lacquer possessing great durability, brilliance and hardness. Discarded picture film scrap is suitable combined with copal or sandarac for this purpose. A representative formula for such a lacquer would be:

1. U.S.P. 1079773, 1914; abst. C.A. 1914, 8, 421.

	Parts by Weight.
Copal	18
Cellulose acetate	10
Tetrachlorethane	33
Ethyl alcohol, denatured	7
Acetone oil, light, rectified	16
Benzol 100%	45

The copal is preferably dissolved in a portion of the tetrachlorethane and all of the benzol mixed, aided if necessary by the heat of a water-bath, the acetate dissolved separately, and the two incorporated.

L. Lederer [1] in 1904 and more recently W. Walker [2] have obtained patent protection for the use of tetrachlorethane as a constituent in acetate lacquers, Lederer's formula being to dissolve one part of acetated cellulose in nine parts of acetylene tetrachloride. Such a lacquer, however, dries too slowly, and is too expensive for commercial work. The observation that copal and other resins are freely soluble in this substituted ethane first made by Lederer has been repeatedly corroborated by subsequent work.

The acetate lacquers of Societe Debauge et Cie,[3] H. Peters,[4] Societe Leduc, Heitz et Cie,[5] are more appropriately described elsewhere.

1. U.S.P. 804960, 1905; abst. J.S.C.I. 1905, **24**, 1314. E.P. 6751, 1905; abst. J.S.C.I. 1906, **25**, 326. F.P. 352897, 1905; abst. J.S.C.I. 1905, **24**, 978, 984; Mon. Sci., 1907, (4), **66**, 33. D.R.P. 175379, 1904; abst. Mon. Sci., 1908, (4), **68**, 43; Zts. ang. Chem., 1907, **20**, 2045; Chem. Centr. 1906,**77**, II, 1544; Jahrsb. Chem., 1905-08, II, 984. D.R.P. 188542, 1905; abst. Mon. Sci., 1910, (4), **72**, 77; Chem. Zts., 1907, **6**, No. 258; Chem. Centr., 1907, **78**, II, 1815; Jahrsb. Chem., 1905-1908, II, 984. For the acetation of cellulose to preserve its structural form in the presence of carbon tetrachloride, see Lederer, Belg. P. 195840, 1906.

2. U.S.P. 1035108, 1912, claim 6 covering the manufacture of solutions suitable for industrial purposes by dissolving acetylcellulose in acetylene tetrachloride. For Lederer vs. Walker on this patent, see **179** Off. Gaz. 851, and **182** Off. Gaz. 511-514.

3. F.P. 418347, 1909; abst. J.S.C.I. 1910, **29**, 1117; 1911, **30**, 96. Addition No. 15217 of 1912 to F.P. 418347, abst. Kunst., 1912, **2**, 316, covers the use of hexachlorethane in tetrachlorethane solution with cellulose acetate for lacquer purposes. For the Chemische Fabrik Griesheim-Elektron method of preparing lacquers, see D. R. Anm. C-22873, 1912; Kunst. 1913, **3**, 479.

4. E.P. 14293, 1910; abst. J.S.C.I. 1911, **30**, 1171.

5. F.P. 429788, 1911; abst., J.S.C.I. 1911, **30**, 1267; Mon. Sci.

The Badische Anilin und Soda Fabrik[1] prepare acetate lacquers and varnishes by employing esters of hexa-hydro phenols, as cyclohexanol acetate, as solvents, either alone or with the addition of other solvents or softening agents. Cyclohexanol formate or acetate, methylcyclohexanol formate or acetate, are said to be cheap, not readily flammable and good solvents of cellulose esters. The solutions dry with sufficient rapidity, and leave the cellulose ester in the form of a transparent, resistant and very elastic coating, which scarcely alters the appearance of the underlying surface. Or,[2] the more readily obtained esters of the cyclopentanols may be employed. Especially is *b*-methylcyclopentanol advocated, this body being an agreeable smelling, colorless liquid which boils at 56°-58° under 14 mm. pressure.

Colored lacquers with an acetate base may be readily prepared by utilizing those basic or acidic dyestuffs soluble in alcohol, as fuchsin, saffranin, naphthol yellow, aurine, bismarck brown, auramine, methyl violets, methylene blues, Victoria green, nigrosines and the indulines. The dyestuffs are dissolved in a small volume of denatured ethyl alcohol, or high grade wood alcohol, filtered from any impurities or undissolved portions, and the desired amount of the concentrated colored solution added directly to the otherwise finished acetate lacquer formula. In the coating of analytical balances, microscopes, spectroscopes or other philosophical or mathematical instruments, dyestuffs of the Soudan series are especially useful, as they combine the various shades represented by the commercial bronzes. Therefore such lacquers may be used to color a brass low in copper to simulate one high in

1913, **78**, 39; C. A., 1912, **6**, 2186; Oil, Paint and Drug Review, Apr. 24, 1912. For resume of use of acetylene tetrachloride in cellulose acetate lacquers containing nothing new, see L. Clement and C. Riviere, Caout. et Guttap. 1912, **8**, 5615-16.

1. D.R.P. 251351, 1911; abst. Wagn. Jahr. 1912, II, 604; C. A. 1913, **7**, 351, 427, 1426; Chem. Tech. Rep. 1912, **86**, 584; Chem. Ind. 1912, **35**, 657; Zts. ang. Chem. 1912, **25**, 2508; Chem. Zentr. 1912, **83**, 1246; Farb. Ztg. 1912, **17**, 2815. U.S.P. 1045895, 1913; E.P. 3869, 7292, 1912; abst. J.S.C.I. 1912, **31**, 1176; F.P. 440733, 1912; abst. J.S.C.I. 1912, **31**, 828; Kunst. 1912, **2**, 414; 1913, **3**, 17; Mon. Sci. 1914, **80**, 14. See also their D. R. Anm. B-64397, 1911.

2. D.R.P. 255692, 1912, addition to D.R.P. 251351, 1911; abst. C. A. 1913, **7**, 1815; Kunst. 1913, **3**, 20.

this metal, the lighter the color of brass the smaller the amount of copper therein. The advantages of the Soudan dyestuffs are their excellent fastness to light. Such lacquers are usually applied by means of an air blast by spraying, in which manner more can be covered in a given time and with greater uniformity and less loss of material. For the coating of small articles as buckles, toys, collapsible tubes and sprinkler tops, the resin lacquers are preferable on account of their low cost. (For nitrocellulose lacquers, see Part III.)

Under the name of "white enamels" are comprised a number of cellulose ester lacquers, containing nitrocellulose and a white pigment, either zinc oxide, or carbonate, less often zinc sulfide, barium sulfate or the product formed by the interaction of barium sulfide on zinc sulfate. At the present time little if any cellulose acetate is being used in this class of lacquers. An inviting field, however, is opened in this direction by the ultilization of uninflammable moving picture film in connection with resins and white pigments of great opacity. The general method of manufacture would be to dissolve the acetate in a high-boiling solvent combination as acetylene tetrachloride and toluol or xylol, pigment being added to the desired color. The pigment is first ground in a mixture of tetrachlorethane and castor oil or tetrachlorethane alone, after which it is added to the acetic ester in solution. A representative formula for this class of lacquers would be as follows:

	Parts by Weight.
Cellulose acetate	14
Tetrachlorethane	42
Denatured ethyl alcohol	8
Toluol	45
Methyl acetone	10
Castor oil	5

Pigment (sufficient) usually about 20 ounces of zinc oxide per gallon. The desirable qualities of a lacquer of this class are considerable strength, smoothness in flowing and slowness and uniformity in drying. Such lacquers find use in the coating of metallic bedsteads, the tipping of the ends of steel

corset stays and the coating of articles of a sanitary nature. Often a double grinding of the pigment is advisable in order to cause it to properly remain in suspension, and bring out the maximum opacity. A trace of methylene blue may be added to apparently increase the whiteness, and resins may be incorporated where a higher gloss is desired. In the coating of corset stays the tips are suspended downwards, the lacquer applied by dipping, the contractility of the lacquer being sufficient so that a noticeable drop is not formed, the end of the stay being rounded off and smooth.

In black lacquers—which may be either glossy or dull—acetate solutions may be mixed with the various spirit-soluble nigrosines where a shiny surface is desired. For mourning jewelry, casket trimmings and for similar purposes where a dull or mat appearance is desired, lamp black previously ground in acetylene tetrachloride and castor oil is added in sufficient proportions to produce the effect intended. Lamp black is exceedingly bulky compared with its weight. Hence progressive grindings is often the most satisfactory way of thoroughly incorporating this pigment in an acetate lacquer formula. Mat blacks are often called wrought blacks from the wrought iron appearance imparted to metal covered with the lacquer.

Cellulose acetate, so far as known, has not been extended to the coating of golf balls, billiard balls, or lacquers imitating the various woods, as mahogany, rosewood, ebony or cocabola. The amount of waste acetate picture film obtainable and its low cost open inviting fields for utilization in this direction, where considerable quantities of the corresponding nitrocellulose solutions have been used for a number of years.

Many of these fields are monopolized by cellulose nitrate solutions simply on account of comparative cheapness.

In the formation of heavy and viscous lac-like coatings from acetylcellulose,[1] acetone or acetic acid solutions are mixed with alcohols, hydrocarbons or other non-solvents, or

1. A. Eichengruen. D.R.P. 254784, 1909; abst. Wagn. Jahr. 1912, II, 604; Chem. Zentr. 1913, 84, 358; Kunst. 1913, 3, 60; 1914, 4, 37; C.A. 1913, 7, 1111. Aust. Appl. 2907, 1910.

liquids which dissolve acetylcellulose in the cold. The solution is then applied to the articles to be coated, and allowed to dry. Or,[1] the acetylcellulose may be dissolved in alcohol in the presence of zinc chloride or ammonium sulfocyanide or potassium sulfocyanide. These solutions remain liquid at ordinary room temperature, and may be used as brush lacquers in the covering of wood or metal. No odor is imparted to the coating due to the relative low volatility of the solvent. The sulfocyanides and zinc chloride, which have a hygroscopic action on the coating, may afterwards be removed by washing with water. These solutions may be used directly for spinning, water being the coagulating medium into which the filaments are forced.

The Chemische Werke vorm. H. Byk have found[2] that esters of lactic acid, particularly methyl and ethyl lactate, are employed as solvents for nitrocellulose and other cellulose esters such as the acetate and formate, and also for certain resins such as copal, sandarac and colophony, in the preparation of lacquers. Such solutions may be diluted with liquid hydrocarbons, more particularly those of the aromatic series, halogen derivatives thereof, ethers, acetone, alcohols, and mixtures of these solvents. For example, 10 parts by weight of acetylcellulose may be dissolved in a mixture of 50 parts by volume of ethyl lactate and 30 parts of benzene; or 50 parts of ethyl lactate, 30 parts of trichloroethylene and 20 parts of alcohol.

1. Bayer & Co. D.R.P. 256922, 1911; abst. Chem. Zentr. 1913, **84**, 1156; Kunst. 1913, **8**, 213; C.A. 1913, **7**, 2116; J.S.C.I. 1913, **32**, 530. See also their D.R. Anm. E-17505, of 1911, being addition to D.R.P. 256922; abst. Kunst. 1913, **8**, 420. According to their D.R.P. 268627, 1911, abst. Kunst. 1914, **4**, 96, alcoholic cellulose acetate solutions may be prepared by the action of stannic chloride (tin tetrachloride) or antimony trichloride (antimonous chloride) upon the alcohol-insoluble cellulose acetates. For instance, if to a solution of 4 parts of stannic chloride in 60 parts of alcohol, there is added 10 parts of acetone soluble acetylcellulose, after standing for some hours, the alcohol soluble modification is eventually formed. Or, 2.5 parts of chloroform soluble acetylcellulose when treated with 50 parts of antimony trichloride in 50 parts of alcohol, gradually becomes soluble in alcohol.

2. F.P. 464617, 1913; abst. J.S.C.I. 1914, **33**, 557; C.A. 1914, **8**, 3364.

According to the Soc. Industrielle des Telephones[1] to a solution, such as is used for coating aeroplane fabric or for electrical insulation, an inert substance is added, for instance barium sulfate, zinc sulfide or oxide, magnesium oxide, etc. Coloring matter may be added and the coating may be varnished after application.

Acetate Bronzing Liquids (Galvano lacs, Ausperite). Thin nitrocellulose solutions intended for application with powdered metals and bronzes, and variously known as Bronzing liquid, Banana oil, Gilding Medium and Chinese, Japanese and Oriental gold paints, have been used for many years as coverings for both wood and metal. They, however, have suffered from various defects which have restricted their use. The aluminum-containing liquids especially when stored in metallic cans spoil in a short time either by the development of acidity or by a coagulation of the nitrocellulose into a form which cannot be brought back into solution by means of solvents. Some of these lacquers are of such thin viscosity as to imperfectly float the bronze, and with these in order to obtain the requisite opacity and covering power a disproportionately large amount of cellulose ester solution is required in order to obtain the proper degree of adhesion.

W. Doerflinger[2] has endeavored to produce a gold paint free from the above enumerated defects by the substitution of cellulose acetate for the corresponding nitrate. The acetate is employed in a volatile solvent combination such as acetylene tetrachloride, alcohol, acetone and benzol, a suitable formula being:

Acetone (substantially anhydrous).....	22	parts by volume
Tetrachlorethane	18	"
Methyl alcohol (substantially anhydrous)	3	"
Benzene 100%.....	55	"
Cellulose acetate (acetone soluble).....	3.5	parts by weight

1. D.R.P. 260915, 1912; abst. J.S.C.I. 1914, **33**, 73.
2. U.S.P. 884475, 1908; abst. J.S.C.I. 1908, **27**, 512; D..R. Anm 23476, 1910. For nitrocellulose-containing bronzing liquid formulas see E.P. 2484, 1878; 22610, 1891; 4169, 1892; 7688, 1892. F.P. 361394, 1906.

The cellulose acetate is dissolved in a mixture of acetone, tetrachlorethane and wood alcohol, and when entirely in solution the non-solvent benzene is added in small portions with much stirring. Bronzes or metals are then preferably incorporated with this to a thin paste in small portions immediately before use. The patentee directs to dissolve 6 ounces of cellulose acetate in 1 gallon of acetone to which 8 ounces of anhydrous sodium carbonate is added. The solvent portion of the above formula is unduly expensive, and the amount of sodium carbonate stated will not dissolve in the quantity of acetone specified. The object of the sodium carbonate is to neutralize any acidity that may be present. Finally 1.5 pounds of bronze powder is mixed with the solution, and the preparation is ready for use. A small amount of castor oil may be added to increase flexibility, and dammar, which is often used in pyroxylin-containing bronzing fluids, is also a useful addition in increasing adhesiveness while at the same time reducing the cost of the finished preparation. The mixed paint is said to keep well in tin cans and other vessels, does not react with the bronze powder or the tin of the cans, works well under the brush and produces a durable and brilliant coat which preserves its luster for a long time. The speed of drying can be varied within great limits by increasing or decreasing the proportion of low-boiling acetate solvent (acetone, b. pt. 56°) or high-boiling solvent (tetrachlorethane, b. pt. 147°).

Imitation Gold Leaf. Recently a number of patents have issued for the use of cellulose esters in the preparation of imitation gold leaf. H. Gregory,[1] J. Fichtmueller,[2] W. Ker,[3] K. Olsen,[4] Kuertz,[5] and A. Huck and L. Fisher [6] have described methods in which cellulose esters are mixed in solution with bronze powders, and this bronzing liquid either distributed over a layer of water in a thin film, or run on a web and after

1. U.S.P. 826781, 1906.
2. U.S.P. 976994, 984805, 1910.
3. U.S.P. 1011443, 1911.
4. U.S.P. 992743, 1911.
5. F.P. 398028, 1908.
6. E.P. 6246, 1901; 17311, 1902.

drying wound up. Shellac, fish glue and other materials have been incorporated with the bronzing liquid in order to aid in adhesion of the gold leaf. In bookbinding, for lettering of titles, and in embroidery and other trimming, it has found an extensive and increasing use. Cellulose acetate is the equal of the corresponding nitrates for this purpose, a satisfactory formula for a gold-leaf composition being:

Acetylene tetrachloride.....	45 parts by weight
Cellulose acetate.....	12 parts by weight
Acetone	15
Benzene 90%.....	40

Bronze, sufficient to impart the consistency and opacity desired.

The cellulose acetate is dissolved in the two solvents, acetone and tetrachlorethane, and the non-solvent benzene added in small portions with stirring.

The bronze is incorporated last and preferably just before use.

Bronzes all contain copper as an essential constituent, which, especially when in a fine state of subdivision, rapidly darkens upon exposure to the air from absorption of hydrogen sulfide and formation of black cupric sulfide. E. Oeser[1] proposes to overcome this tendency to darken by mixing the pulverized metal with a rapidly drying lacquer as cellulose acetate in acetone and then spraying the mixture under pressure in a closed chamber, where with proper temperature and ventilation, it is said to drop to the bottom as a powder. Each minute particle of metal is thus encased in a water-repellant cellulose acetate envelope and hence is protected from atmospheric action.

Gilded Lace. In the method of J. Daly[2] cellulose esters dissolved in appropriate solvents, i. e., nitrocellulose in amyl acetate, or cellulose acetate in tetrachlorethane and methyl alcohol, are worked up into a paste with bronze powders. The fabric to be treated is then saturated with this mixture and dried, metal being thereupon deposited by electrolysis.

1. U.S.P. 976594, 1910.
2. U.S.P. 694946, 1902; abst. J.S.C.I. 1902, **21**, 474.

The process is said to be especially applicable to the preparation of silvered and gilded lace.

In another method [1] the lace is coated with an acid resisting varnish, such as cellulose acetate lacquer, and before the solvents have entirely evaporated, the fabric is covered with bronze powder or other finely divided metal. The two operations may be combined by mixing the bronze with the lacquer to a homogeneous mixture. The excess of varnish is afterwards removed by means of a blower, when the meshes of the lace will be left open and distinct, although the threads are coated with the divided metal and stiffened by the lacquer. The next step is the electro deposition of the desired metal upon the impregnated fabric, this being accomplished by attaching the lace to a wire cage, a coil of copper wire being wrapped around it, and the whole immersed in the electroplating fluid. After the electro-deposited metal has been rendered compact by brushing or rolling, the lace is again immersed in the bath and covered with a deposit of precious metal. Gold is to be used where the flexibility of the lace is to be retained, silver and copper imparting stiffness to it.

Treating Linen with Cellulose Acetate. The process of A. Zimmer [2] has for its object the application to the surface of the fabric a glazed and washable exterior sufficiently waterproof to withstand chemical action set up by perspiration and the action of the atmosphere, without at the same time detracting from the characteristic linen appearance. To this end the starched and ironed fabric is coated with a solution of cellulose acetate in a mixture of trichlorethane, trichlorethylene, castor oil and camphor, or alternately with a solution composed of cellulose butyrate in a mixture of acetone, trichlor-

1. E.P. 5348, 1902; abst. J.S.C.I. 1902, **21**, 912. According to an alternate method, the lace is stretched in a frame and brushed over with lacquer, silver sulfide being subsequently precipitated upon it by successive treatment with solutions of silver nitrate and a soluble sulphide. See also J. Daly, U.S.P. 707306, 1902; abst. J.S.C.I. 1902, **21**, 1186.

2. E.P. 12406, 1910; abst. J.S.C.I. 1911, **30**, 206; D.R.P. 242786, 1910; abst. C.A. 1912, **6**, 2182; Wagn. Jahr. 1912, II, 509. In the apparently corresponding U.S.P. 1025731, 1912; abst. C.A. 1912, **6**, 1994, nitrocellulose is claimed, specified and described to be used the same as in the English and German patents above cited for the use of cellulose acetate.

ethylene, castor oil and camphor. After the coating has been applied and the articles allowed to dry, they are finished by polishing with successive applications of powdered pumice stone, talc and chalk.

In waterproofing collars, cuffs, shirt fronts, table cloths and similar linen fabrics, and to obtain a coating which is not friable, substantially waterproof, relatively uninflammable and retains indefinitely its white color, H. Peters [1] proceeds as follows. The fabric is first coated with a solution consisting of calcium or barium carbonate and zinc sulfide,—either with or without barium sulfate—admixed with sodium-casein (sodium 6%, casein 94%) in 200 grms. of hot water mixed with 30 grms. methyl aldehyde (oxymethylene) to produce a liquid of the consistency of thin cream. Coagulation may be guarded against by the addition of 15-20 grms. of glycerol. The article to be waterproofed is first dipped in the above solution, dried, then dipped in either a solution of 100 parts trinitrocellulose dissolved in 22 parts of amyl ether and 22 parts of monochloracetic acid or chloramyl (amyl chloride) diluted with 150 parts of amyl alcohol. Or the second coating may comprise 100 grms. triacetylcellulose dissolved in 1.5 liters of methylated ether diluted with 2 liters of amyl alcohol, chloracetic acid or nitrobenzene. A small quantity of methyl or amyl silicates may be added to still further decrease the inflammability. The elasticity of the coating is increased by the addition of 2% of castor oil. In the case of waterproofing table cloths, where a high degree of flexibility is required, a final treatment with castor oil under pressure rollers is recommended.

In another process,[2] starched linen is rendered waterproof by treatment with a first coat of a 20% solution of cellulose acetate with or without the addition of camphor, and after drying, a final coating of nitrocellulose in solution is applied.

In the M. Kruemmling method,[3] paper, pasteboard, card-

1. E.P. 870, 1910; abst. J.S.C.I. 1911, 30, 206; F.P. 420127, 1910; abst. Mon. Sci. 1913, 78, 21; J.S.C.I. 1911, 30, 280. See also H. Peters, E.P. 14293, 1910; abst. J.S.C.I. 1911, 30, 1171.

2. Madam Roggenkaemper, nee E. Vahlkamp, F.P. 407932, 1909; abst. J.S.C.I. 1910, 29, 623.

3. E., 10578, 1909. Cites E.P. 14488, 1903; 4957, 26502,

board, linen or canvas wrappers are rendered capable of resisting external influences, by impregnation with a solution containing as main ingredients, commercial cellulose acetate dissolved in alcohol, acetone or glacial acetic acid. The wrapper may afterwards be pressed, stamped, ribbed or printed upon by the use of an ink containing a cellulose acetate solvent such as glycerol triacetate, ethylene glycol diacetate, resorcinol diacetate or similar viscous liquids which act as direct solvents in the cold for partially hydrated cellulose acetate.

The lacquer patented by Leduc, Heitz & Co.,[5] composed of acetone-soluble cellulose acetate in tetrachlorethane, alcohol, chlorohydrins and acetone, is claimed as specially suitable for waterproofing textiles. For printing upon textiles with cellulose acetate see Sericose.

According to A. Douqué, who has patented a process for so doing,[6] washable linen may be made waterproof by first applying to the fabric a basic aluminum acetate in solution, in which the proportion of aluminum corresponds with the formula $Al_2(OH)_2(C_2H_3O)_4$, this substance possessing the property of being decomposed when heated to a temperature such as that to which the linen is submitted in the ordinary ironing process, thereby depositing in the interstices of the fabric an insoluble aluminum compound substantially waterproof. The fabric is then impregnated with cellulose acetate dissolved in chlorhydrin or other suitable solvent, or preferably first with a 3%-5% solution of cellulose acetate, then dried and followed by a final coat of nitrocellulose or celluloid of the same strength. Starch may be added to the aluminum salt in the first coat and softeners, as castor oil, may be incorporated in the cellulose ester finishing coat. The patentee claims that linen prepared in the above described manner

1906. For process of waterproofing linen with nitrocellulose, see W. Brueckner, D.R.P. 238361, 241781, 1909; abst. C.A. 1911, **5**, 2960; 1912, **6**, 2180; J.S.C.I. 1912, **31**, 227.

5. F.P. 429788, 1911; abst. J.S.C.I. 1911, **30**, 1267; C.A. 1912, **6**, 2186. They are said to produce a lacquer (Belg. P. 229396) especially suitable for the coating of aeroplane wings and called by them Emaillit (Kunst. 1912, **2**, 419).

6. E.P. 17449, 1909; abst. J.S.C.I. 1910, **29**, 1007. F.P. 403761, 1909; abst. J.S.C.I. 1910, **29**, 19.

appears like well-washed ordinary linen, is proof against sweat and dampness, does not readily soil, and can easily be washed with water.

In the process of E. Girzik for waterproofing articles by impregnation,[1] cellulose compounds as the acetate are rendered more highly water-repellant by the addition of castor oil or stearic acid, which also removes the adhesive properties.

The Viscose Development Co. produce permanent coatings by spreading a solution of cellulose acetate upon a form, which is then subjected to the action of water or an aqueous solution such as glycerol. The resulting hollow body, when applied as a coating, is exposed to the air, as the result of which the moisture evaporates off, yielding a permanent waterproof coating of cellulose acetate.[2]

Cellulose Acetate Imitation Leather. The nitrocelluloses have long been used for the production of artificial leather, by the coating of cloth with mixtures of inflammable cellulose ester, oils and pigments, afterwards embossing the properly coated cloth in order to imitate the grain of the hide of various animals. The cellulose acetates, while applicable for this artificial leather manufacture, have been unable to satisfactorily compete with the nitrocellulose leather on account of the cost of the cellulose acetate. The large amount of waste uninflammable film now available in certain sections gives added interest to this branch of the cellulose ester art, as it furnishes a supply of cellulose acetate which is continually increasing in bulk, and which is entirely suited for the coating of cloth and the finishing into imitation leather.

The film stock as received contains silver, gelatin and sometimes a light coating of cellulose acetate or nitrate to waterproof the gelatin layer. The gelatin may be separated as described elsewhere. The film thus obtained is first preferably dried, especially if the gelatin was removed by a process introducing water, after which the acetate film with the appropriate solvent and nonsolvent fluids, is introduced into a mechanical mixer and agitated until entire solution. Pigments

1. Aust. P. 3034, 1913; abst. C.A. 1914, 8, 2229.
2. D.R.P. 270314, 1911; abst. C.A. 1914, 8, 2251, 2252.

added for coloring purposes are first ground in a mixture of tetrachlorethane and castor oil, the latter being added to increase the pliability of the finished product. A representative coating composition for artificial leather formation would be:

Cellulose acetate.....	11	parts by weight.
Tetrachlorethane.....	45	parts by volume.
Acetone oil light.....	10	"
Benzol 90%.....	45	"
Castor oil.....	9	"

The acetate is dissolved in the tetrachlorethane and light acetone oil, and the castor oil in the benzol, together with any pigment which may previously have been ground in the oil. The latter mixture is then added in small portions to the former, and agitated until a homogeneous mass results. The dope or coating composition is then spread on cloth under tension in one or more coats, dried between each application, and after thorough expulsion of the solvent, is embossed by roll or plate presses with the appropriate design. If a gloss is desired the final coat is low in pigment and high in cellulose acetate and tetrachlorethane, or the final coat may be a colorless acetate lacquer, in which instance the maximum gloss is imparted to the fabric. The preparation of antique or hand decorated leather, and the application of smootching and other processes in order to obtain especial effects may be made in the same manner as now carried out with the pyroxlin leathers. Spanish and mission leather, which is devoid of gloss and used for mission furniture and other severe upholstery, comprises the application of a colored cellulose ester lacquer over deeply embossed artificial leather. The object of the treatment is to give to the leather the appearance of much wear and great age from the apparently worn appearance of the surface. Smootching is the opposite, for here the colored lacquer is applied to the surface only of the embossing, the object being to more nearly imitate the appearance of natural hides. It will be remembered that natural hippopotamus, alligator, rhinoceros, elephant and similar hides are all darker on the surface than in the folds of the

skin, and it is to more nearly duplicate the natural appearance of these skins that the embossed patterns are rubbed over on the surface only with a lacquer darker in color than the artificial leather being treated.

The substitution of cellulose acetate for pyroxylin would remove the greatest objection to this class of imitation coverings—the inflammability due to the cellulose nitrate.

L. Lilienfeld [1] has described the manufacture of artificial leather of the type in which a material such as textile fabric, paper, or the like, is provided with one of more coatings of a cellulose-ester compound, such as celluloid, and a softening agent, substituting, wholly or in part, for the oils or fats previously used as softening agents, a phenol ester remaining liquid at 0°. Coatings of the above described nature may be alternated with layers of a mixture of viscose and the products obtained from Chinese wood oil and aromatic amines, according to the process of E. P. 636, 1910. The cellulose ester compound such as celluloid, is dissolved in a suitable solvent, and a phenol ester which remains liquid at 0°, such as *o*-tricresyl phosphate, is added. This solution either alone or mixed with binding agents such as acetylcellulose, formylcellulose, caoutchouc, gutta-percha, drying oils, etc., or with filling substances such as ground leather, powdered cork, asbestos, chalk, kaolin, or with pigments, coloring matters, or other softening agents, such as castor oil, glycerol, sugar, or soap, is applied on textile fabrics, paper, or cotton or paper fleece, in one or more layers. The viscose compound is prepared by kneading together viscose, or a dissolved heavy metal salt of viscose such as a zinc compound, with the products obtained

1. U.S.P. 1090730, 1914; abst. C.A. 1914, 8, 1680. E.P. 28210, 1912; abst. C.A. 1914, 8, 1886. Lilienfeld (E.P. 23892, 1901; abst. J.S.C.I. 1902, 21, 771. F.P. 316229; abst. J.S.C.I. 1902, 21, 704) obtains impressions with pigments and powdered metals which are said to be perfectly resistant and pliable, by the use of (1) metallic salts of fatty acids, especially the oleates, stearates and palmitates of aluminum and zinc, and metallic resinates, dissolved in volatile or non-volatile oils, benzene, carbon bisulfide, or acetone; (2) acid derivatives of albumin, e. g., acetyl-albumin (obtained by treating albumin with acetic anhydride and a condensing agent or with acetyl chloride) dissolved in acetone or ethyl acetate; and (3) india-rubber or gutta-percha, decomposed by heating for about 5 hours at 240°-300° with a drying oil.

from Chinese wood oil, aromatic amines, and a condensing agent. A solution of emulsion of such products prepared with the help of alkalis, soaps, or alkali salts of the fatty sulfo acids, and water may be used. This compound, together with filling substances such as those mentioned above, and other binding agents such as glue, albumin, caoutchouc residue or drying oils, and with softening agents, is applied in layers alternating with the cellulose-ester compound. One example of the cellulose ester compound is: alcohol 60, acetone 30, powdered celluloid 10, and *o*-tricresyl phosphate 10. Other phenol esters which may be used are creosote phosphate, carbonate, and oleate. The viscous compound is prepared by mixing specified proportions of Chinese wood oil, *o*-toluidine, zinc chloride, soda-Turkey-red-oil, soda solution, and water. After being applied, the viscose in this layer may be rendered insoluble by any known means. The final product may be calendered or marked with any suitable design.

According to the Raison Sociale Siebert, who have patented a process for so doing,[1] waxed cloth and paper may be satisfactorily prepared by the use of cellulose acetate as a substitute for fats, oils or paraffin hydrocarbons, the method being to first cover the paper or cloth with successive thin layers of boiled linseed oil with drying after each application. Cellulose acetate in solution is next applied, either alone or mixed with drying oils, the final coat being a varnish of transparent cellulose acetate. After the final drying the material is embossed or otherwise ornamented and may be printed. For colored waterproof effects acetate lacquer may be dyed with basic dyestuffs previously brought into solution by means of alcohol, the oil coats being dispensed with. Methyl green, Victoria green, aurine, auramine, methyl blue, methylene blue or violet, fuchsine, saffranine and rhoduline heliotrope are examples of suitable dyestuffs.

In the W. Balser process,[2] fabrics are rendered impermeable to the action of Roentgen rays by adding to the fabric

1. F.P. 396467, 1908; abst. J.S.C.I. 1909, **28**, 598.
2. D.R.P. 202267, 1906; abst. C.A. 1909, **3**, 492; Chem. Zentr., 1908, **79**, II, 1399.

as a coating composition an acetone-soluble cellulose acetate to which has been added certain heavy metallic oxides in a fine state of subdivision. Or, it is claimed, the coating composition may be drawn into artificial filaments and then woven into designs.

In the manufacture of cellulose acetate artificial leather, the minimum of solvent may be used by taking the hydrolyzed cellulose acetate, still in the acetating mixture and at the point where the partial hydration has proceeded to the desired length, and instead of precipitating the ester with water, cloth is coated with this viscous mixture, to which may be added pigments or dyestuffs which are unaffected by glacial acetic acid or the catalyzer used. The coated cloth is first passed through water to wash out all traces of acid, then over steam rolls until dried, after which it is exposed to solvent either by spraying the solvent onto the coated surface, or by rapidly passing the cloth through a bath of solvent. In this manner the entirely softened acetated cellulose layer is next brought under calender embossing rolls or embossed in a plate press, when the material is ready for the trade.

Cellulose Acetate Compound Fabrics, such as described by the Soc. Anon. des Celluloses Planchon,[1] may be prepared by spreading a cellulose acetate solution on a polished surface and allowing the solvent to evaporate, after which a suitable textile fabric such as tulle is moistened with a solvent of cellulose acetate, and the textile incorporated with the film by applying one to the other under pressure. The compound fabric is then stripped from the polished surface. Artificial foil is made by these patentees[2] by converting artificial hair into foil by passing between rollers such as are used for the manufacture of metal foil.

A. Eichengruen[3] first produces a long film or sheet of

1. E.P. 7442, 1911; abst. J.S.C.I. 1912, **31**, 224. See also E.P. 4959 ,1910; abst. J.S.C.I. 1911, **30**, 19. See Aktien Ges. f. Anilinfabr, E.P. 21015, 1913; F.P. 461058, 1913; abst. J.S.C.I. 1914, **33**, 350.

2. F.P. 410721, 1909; abst. J.S.C.I. 1910, **29**, 811.

3. E.P. 4959, 1910; abst. J.S.C.I. 1911, **30**, 19. F.P. 413901, 1910; abst. J.S.C.I. 1910, **29**, 1101. D.R.P. 229450, 1909. Aust. Anm. A-2906, 1910.

acetylcellulose, and then attaches this to the textile by means of a solvent aided by pressure. For imitation leathers this process has, with nitrocellulone, proven a failure for the reason that the sheets never adhere as firmly to the textile as when the latter is treated with the ester in solution, which enables the viscous cellulose acetate solution to penetrate the interstices of the fabric and anchor firmly therein. This method, so the patentee claims, is valuable for the preparation of variegated, frosted or patterned effects, the solution being allowed to dry upon a rigid surface containing the pattern, and when dry is peeled off, the obverse side being then used as the outer or upper side when attached to a fabric or other support.

In an attempt to reduce the cost and simplify the manufacture of imitation leather from uninflammable cellulose esters, it has been proposed to take the acetylated cellulose while still in solution in the acetating bath, i. e., use the acetating bath with the ester dissolved therein as a lacquer, and spread this on cloth in the usual manner. Care must be exercised in coating cotton with such a mixture on account of the solvent action of the constituents of the acetating bath upon the cotton textile. After coating, the cloth is immediately passed through a 3%-5% aqueous solution of sulfuric acid to partially hydrate the coating to the acetone-soluble modification. After drying, the cloth is exposed to the vapors of a solvent of the acetated cellulose, and then embossed in the usual manner.

In the manufacture of designs of metals and colors on fabrics, paper, glass and metals—the production of so-called metallized fabrics—F. Bayer & Co.[1] suspend finely divided metal particles, earths or lakes, in readily congealing fluids, which are mixed with readily magnetisable metals with or without the addition of colloids. This mixture is allowed to congeal, evaporate or solidify upon the fabric provided with the design in thin layers. This process takes place under the influence of a suitable arrangement of magnet, whereby many

1. D.R.P. 235381, 1911; abst. Wagn. Jahr. 1911, II, 533. In this connection see F. Bayer & Co., D. R. Anm. F-27152, F-27686, of 1909.

curious and intricate designs result. Very beautiful designs may be produced by the use of gold bronze incorporated in a 5% solution of acetylcellulose suspended together with finely powdered metallic iron.

A process has recently [1] been described for the fireproofing and waterproofing of fabrics for flying machines and balloons, washable linen, etc., by treating the fabrics with fatty acid esters of cellulose together with fireproofing substances such as salts of boric, sicilic, sulfuric and tungstic acids, or their phenyl esters, or non-inflammable chlorine derivatives of aniline. The fireproofing substances may be applied either before or after the ester solution, or in the form of dust, which is then fixed. A softening agent may often be added to the ester solution with benefit.

In the G. Gawlich method [2] the agglutinant is placed on the fabric in dry or moderately wet condition, but not dissolved, being afterwards placed in solution by treatment with steam, gaseous or vaporous solvent. Preferably a layer of finely powdered celluloid, cellulose acetate, or the like, pure or mixed with fillers or loading, dry or wet with non-dissolving, indifferent fluids, is spread on the material, and the whole treated with solvent.

K. Goldstein [3] manufactures waterproof, noninflammable impregnated asbestos fibers, textiles and fabric by covering the asbestos by solutions of acetylcellulose to which may be added talc, kaolin or other indifferent substances.

A process has been introduced by the Societe Ballaud et Cie which depends for its merit upon the claims of decreasing the cost of cellulose acetate films and filaments by first producing a film or filament of a less expensive material, such as gelatin or viscose, then treating this with a plurality of thin coatings of an acetate lacquer, the number of coats required

1. A. Eichengruen, E.P. 7418, 1913; 7899, 1914; abst. C.A. 1914, **8**, 2490, 3124; J.S.C.I. 1914, **33**, 478. F.P. 455811, 1913; abst. J.S.C.I. 1913, **32**, 939. Aust. P. 57984; abst. Kunst. 1913, **3**, 218. See also Eichengruen, D.R. Anm. E-14210, E-14630, 1909.

2. E.P. 16199, 1909; abst. J.S.C.I. 1910, **29**, 420; Aust. P. 46036.

3. D.R.P. 219116, 1908; abst. C.A. 1910, **4**, 2048; Chem. Zentr. 1910, I, 970.

depending upon the extent of waterproofing effect desired, and the concentration and viscosity of the acetate lacquer.[1]

Coating of Skins with Cellulose Acetate. The advent of the leather splitting machine making it possible to split a natural hide into three or four pieces each of the same area as the original skin, opened up great possibilities for the utilization of thin and inferior leather in the production of merchantable articles. The three sections in which a hide is ordinarily split are usually called the buff split, the grain split and the flesh split, the latter being next to the flesh of the animal and the first being on the exterior, or hair side. As in the formation of artificial leathers, the greatest factor in impeding progress in this field has been the higher cost of cellulose acetate over the corresponding nitrate, without the acetate imparting sufficiently distinctive merit to overcome the higher cost.

The leather ornamenting and coating processes of W. Field,[1] A. Kennedy,[2] B. Goldsmith,[3] Adams and McKay,[4] M. Knaster,[5] L. Feval [6] and M. Pianko [7] are all adaptable to the use of cellulose acetate. In the employment of acetylcellulose coating compositions for the manufacture of patent and enameled leather, more experimental work has been done, but the art at the present time cannot be said to be established on a firm commercial basis, at least in the United States. The difficulties to be overcome in obtaining the best results are in the main the same as with attempts to use nitrocellulose for the same purpose. The strength, flexibility and elasticity of cellulose acetates in leather coating is not the equal of the nitrocelluloses in the author's experience. The cellulose acetates do not appear to possess the lasting qualities in wear under various climatic conditions and do not satisfactorily respond to the rigid tests met by nitrocellulose. In miscibility

1. F.P. 457925; abst. Kunst. 1913, 8, 476.
1. U.S.P. 627493, 1899.
2. U.S.P. 587097, 1897.
3. U.S.P. 909288, 1909.
4. U.S.P. 789249, 1905.
5. E.P. 28743, 1907; F.P. 385900, 1908.
6. U.S.P. 848357, 1907.
7. E.P. 9304, 1902.

with linseed and other drying oils no difficulty has been experienced, but in adhesion to the leather and the ability to withstand abrasive wear, the acetates, so far as the author is aware, are not sufficiently satisfactory. In the coating of furs and skins little, if anything, has been done. The transition stage through which cellulose acetate is passing commercially is not sufficiently far advanced in some lines to admit of accurate comparisons with the older established nitrocellulose industry, and the leather industry is a field which has as yet been but superficially covered.

In the stiffening of hats, felt, feathers and braid, the Maysers Hutfabrik [1] take the dyed hat or other article in the rough, stiffen the rim portion with shellac, then bring onto the form where it is shaped up, and finally waterproof by impregnating the crown with a suitable solution of cellulose acetate or nitrate.

Artificial Bristles. Natural animal bristles are becoming more expensive and difficult to procure, but are still generally used in the manufacture of brushes, brooms and polishing wheels. B. Borzykowski has described in a vague manner [2] the formation of artificial bristles from cellulose acetates, in which after the usual acetylation process, the mass is either projected through orifices into coagulating media to directly form the bristles, or a solid mass is made, seasoned, and from the block so formed bristles are planed off and afterwards shaped. This method offers the added advantage that the bristles so formed are white in color, whereas it is a difficult and unsatisfactory process to bleach animal fibers without affecting their elasticity or tensile strength. Water, benzine, benzene or turpentine are suitable precipitating media, the filaments being left in the coagulating bath until the acetating constituents have been removed. The formed bristles may be dyed to resemble the hair of various animals by methods described under Dyeing. It must be stated that all such fibers which the author has examined have been deficient in strength,

1. D.R.P. 273979, 1913; abst. C.A. 1914, **8**, 3124.

1. U.S.P. 1010222, 1911; abst. J.S.C.I. 1912, **31**, 24. F.P. 424428, 1910; abst. J.S.C.I. 1911, **30**, 740.

so that in wearing they do not successfully compete with the natural bristles.

Preservation of Documents with Acetate Lacquers. In the pyroxylin solutions has often been resorted to. In engravings, action of the elements, impregnation of the paper with pyroxylin solutions has often been resorted to. In engravings, maps or stenciled work no especial precautions in lacquering are necessary, but in the more important written documents where India ink is used, especial precautions are required. The nitrocellulose lacquers have been objected to as unsuitable on account of the possibility of the liberation of free nitric acid and its effect upon the document. To obviate this possibility of paper or parchment deterioration, the cellulose acetate lacquers have been advocated.

A. Martens [1] has experimented with acetate lacquers with satisfaction, and recommends cellulose acetate dissolved in a mixture of alcohol, ethyl acetate, ethyl aceto-acetate and camphor, a preparation supplied under the name of "Cellit" varnish. Schlutting [2] has raised objection to its use on account of its supposed acid reaction and the reddish cast to the dried film. The tendency toward acidity can be entirely obviated in a properly prepared acetate lacquer, and the reddish tinge, possibly due to the use of iron utensils, might be overcome by storage in glass containers. Such a lacquer, of course, would be unsuitable for the coating of collodion-coated photographic papers, due to the mutual solvent action of ethyl acetate upon the cellulose nitrates and acetates. Traces of acidity from ethyl aceto-acetate would have little or no effect upon the paper of documents.

H. Frederking [3] as the result of his experiments concludes that no fear need be entertained as to the possible injury of documents preserved with acetate lacquer.[4] The speed of

1. Mitt. kgl. Matieralprufungsamt, 1911, **29**, 57; abst. J.S.C.I. 1911, **30**, 414; C.A. 1911, **5**, 2943.

2. X Deutschen Archivtag in Posen "Mitteilungen" 1911, Part 2, 57.

3. Mitt. kgl. Matieralprufungsamt, 1911, **29**, 360; abst. J.S.C.I. 1911, **30**, 1307; C.A. 1912, **6**, 421; Chem. Zentr. 1911, (5), **14**, 1892; Zts. ang. Chem. 1912, **25**, 1549.

evaporation of lacquers intended for document preservation may be modified within wide limits by the proper selection of the solvent or solvents used. In the preparation of carbon papers and stereotype paper, the paper is coated with a wax or paraffin composition containing the coloring matter. To reduce the tendency to rub off and "smut" such papers may be given a light coat of acetate lacquer. With legal papers whose authenticity is called in question before the Courts, and which are made the basis of examination and testimony, it is often desirable to coat the document (a will, for instance) before the instrument is turned over to the handwriting and ink experts, that no dirt or other marks may come in contact with the paper surface during what may be extended microscopical examination, and the unavoidable handling which such an instrument undergoes when offered in evidence. A cellulose acetate lacquer would be suitable for this purpose.

Artificial Filaments from Cellulose Acetate,[1] more often

4. See also Chem. Ztg. 1910, **34**, 1344.

1. For general articles on cellulose acetate filaments, see R. Bernard, Mon. Sci. 1905, 321; Zts. ang. Chem. 1906, **19**, 86; Jahr. Chem. 1905-8, 989. F. Beltzer, Mon. Sci., 1910, (4), **24**, 145, 162; abst. Chem. Abst., 1910, **4**, 1238; Chem. Zentr. 1910, **81**, 11, 509. H. Chauvet, Bull. Technologique, 1912, No. 5, 679. A. Colin, Rev. gen. Chim., 1909, **12**, 49-62; abst. Chem. Zentr., 1909, **80**, I, 1121; Zts. ang. Chem., 1909, **22**, 943, 1620; A. Colin, Rev. gen. Chim., 1909, **12**, 95-95; abst. Zts. ang. Chem., 1909, **22**, 1620. Rev. gen. de Chim. pure et appl. 1909, **12**, 95. W. Doht, Zts. ang. Chem., 1907 **20**, 743-746; abst. C.A. 1907, **1**, 1359, 2179; Bull. Soc. Chim.. 1907, (4), **2**, 908; Jahrsb. Chem., 1905-08, II, 983; Chem. Centr. 1907, **78**, I, 1736; W. Dreaper, J.S.C.I. 1909, **28**, 1297-1303; abst. Bull. Soc. Chim., 1910, (4), **8**, 524; C.A. 1909, **3**, 490; Chem. Zentr. 1910, I, 1396; Zts. ang. Chem. 1910, **23**, 959. W. Dreaper and J. Davis, Jour. Soc. Dyers 1909, **24**, 294; abst. C.A. 1909, **3**, 490; J.S.C.I. 1909, **28**, 19. E. Fischer, Kunst. 1912, **2**, 21-24, 48-52, 64-69. A. Herzog, Chem. Ztg. 1910, **34**, 347-349; abst. Zts. ang. Chem., 1910, **23**, 1390; J.S.C.I. 1910, **29**, 585; Jahr. Chem. 1910, 428; C.A. 1910, **4**, 2371. H. Lebach, Chem. Ztg. 1911, **35**, 107. R. Loewenthal, Chem. Ztg. 1909, **33**, 753-755, 770-772; abst. Bull. Soc. Chim., 1910, (4), **8**, 59. W. Main, Chimiste, **3**, 41-43, 43-45; abst. C.A. 1912, **6**, 1849. W. Massot, Zts. ang. Chem., 1905, **18**, 1090-1098; abst. Wagn. Jahr. 1905, II, 397; C.A. 1907, **1**, 2493; Zts. ang. Chem., 1908, **21**, 340-354; abst. Bull. Soc. Chim., 1908, (4), 635; Zts. ang. Chem., 1907, **20**, 437-444, 484-490; abst. Bull. Soc. Chim., 1907, (4), **2**, 903. Zts. ang. Chem. 1909, **22**, 241-252, 299-305; abst. Bull. Soc. Chim., 1909, (4), **6**, 556. Marsden, Farb. Ztg., 1906, **42**, 172. E. Thiele, Chem. Ztg., 1904, **28**, 715-721. See also Wagn. Jahr. **48**, 730-734; **45**, 1064; **47**, II, 611; **50**, II, 394; **56**, II, 434. In "Encyclopedie der Tecknischen Chemie," vol. 1, pp. 114-130,

called simply "Acetate Silk," differ from all other classes of artificial filaments in the following five distinct respects: (1) The filaments are composed of an ester, and are not a form of cellulose modified or degraded by a cycle of chemical changes through which it has undergone in the various manufacturing steps incident to its production from the original cellulose to the finished thread. (2) It is distinguished from all other "silks" by its very low density, which is very close to 1.25. From this it follows that a given unit weight of cellulose acetate will produce a greater number of lineal feet of filament of a given dameter. (3) Both the normal atmospheric moisture contained therein, and the hygroscopicity of the filaments is less than other artificial fibers, these properties being of distinct technical advantage in weaving and the preparation of textile fabrics. (4) When wetted with either cold or hot water, the distortion, swelling and relative loss in tensile strength is less than with other fibers, and any distortion, swelling or weakening is but temporary during the wetted state. This is of especial importance in dyeing. (5) Nitrocellulose silk loses the weight of the entire nitric acid radical due to denitration; viscose filaments decrease in weight from volatilization of carbon disulfide and the solution of salts in the coagulating bath; cuprammonium-cellulose fibers become lighter from solution of copper and elimination of ammonia. With these three classes of artificial filaments, therefore, the final weight of merchantable fiber is

is a general article on acetylcellulose by A. Eichengruen. F. Marsden, Jour. Soc. Dyers Col., 1905, 21, 102, 192. A. Eichengruen, Kunst. 1911, 1, 452. Zts. ang. Chem., 1908, 1730; abst. Wagn. Jahr. 1908, II, 500. L. Clement and C. Riviere, Rev. chim. Ind., 22, 215-20; abst. C.A., 1911, 5, 3908; W. Walker, Jour. Frank. Inst., 1907, 144, 131-140; abst. C.A. 1908, 2, 318, 2619. F. Beltzer, 8th Intl. Cong. Appl. Chem., 1912, 8, 13; Mon. Sci. 1911, (5), 74, 641.

W. Massot, Farb. Ztg., 1909, 18, 146, 166, 182; Zts. ang. Chem. 1909, 22, 241, 252, 299, 305; Chem. Zentr. 1909, I, 801; Bull. Soc. Chim. 1909, (4), 6, 555.

A. Herzog, Zts. ang. Chem. 1906, 19, 1899; Oest. Chem. Ztg. 1906, 9, 166; Jahr. Chem. 1905-8, II, 4624; Chem. Zentr. 1906, 77, II, 372.

C. Hassack, Oest. Chem. Ztg. 1900, 3, 235, 267, 297; Chem. Zentr. 1900, I, 1312; II, 226, 359.

Saget and Suevern, Bull. Soc. d'Encouragement, 1906, 540.

little more, if any, than the original weight of the cellulose from which they were prepared. On the other hand, with acetate silk the acetic acid radical remains attached and is conserved, and the maximum weight is attained in the finished product. Assuming a C_6 molecule for cellulose, its esterification into a tri-nitric ester involves a gain in weight from 162 parts to 297 parts, or an apparent increase of 83%, yet in the subsequent elimination of the inflammability by denitration the nitrogen is usually reduced to less than 0.3%, from which it appears that there is no gain in weight when cellulose is transformed into denitrated nitrocellulose silk. Similarly when cellulose is acetylated to the triacetate, the change of 162 parts of cellulose to the normal triacetate gives a theoretical weight of 288 parts, or an apparent gain of 78%. Partial hydration subsequent to acetylation does not materially affect this yield, so that, including the addition of certain softeners and plastic-inducing bodies which are added, an actual gain in weight of 75% is substantially approached in practice. Therefore, although the initial cost of cellulose acetate manufacture is high as compared with the formation of nitrocellulose silk, the finished yield is as 100 to about 175 in favor of the acetylcellulose. The fact that a lower nitration than the trinitrate is actually produced in practice, does not change in any way the ratio of the above comparison.

The manufacture of artificial filaments from cellulose acetate first received protection in the United States in 1902,[1] the details of the process being disclosed in 1905.[2] In carrying out this invention the patentees first dissolve the cellulose ester in chloroform, in the proportion of 100 gms. of acetate to 1000 gms. of chloroform, to which has been added 50 gms. of cresol, phenol or body having similar softening effect. After the acetate has passed entirely into solution a mixture of 50 gms. of oleic acid dissolved in 200 gms. of chloroform is

1. Mork, Little and Walker, U.S.P. 712200, 1902; abst. Mon. Sci., 1903, (4), **60**, 165. The material used was preferably prepared according to U.S.P. 709922, 1902; E.P. 20660, 1902; F.P. 324862, 1902; abst. J.S.C.I. 1902, **21**, 1345; 1903, **22**, 646, 1011.

2. Mork, Walker and Little, U.S.P. 792149, 1905; abst. J.S.C.I. 1905, **24**, 799; Mon. Sci., 1906, (4), **64**, 22.

then added, and the solution carefully filtered from undissolved or partially dissolved particles. The threads or filaments constituting the artificial silk are then formed from this solution by projecting it through fine orifices into an appropriate coagulating medium, the latter being any suitable fluid which will dissolve the chloroform or volatile solvent portion of the acetate solution. The petroleum naphthas, terpenes as turpentine, camphor oil and the commercial benzols, toluols and xylols are among the precipitating fluids found valuable. After formation the filaments are united into threads by twisting, wound upon reels, and subsequently treated in a similar manner to the finishing of natural silk fibers.

In 1903 L. Lederer [1] published his process for the formation of variously shaped industrial objects from cellulose acetate, in which is described the formation of filaments by projecting an acetic acid solution of the acetate into alcohol as the coagulating fluid. However, any liquid miscible with the solvent of the acetylated cellulose which does not dissolve the latter is an acceptable precipitant. The Farbenfabriken vorm. F. Bayer and Co. eliminate the necessity for the use of a coagulant and at the same time recover the acetate solvent,[2] by forcing a 15% solution in chloroform through a capillary tube into a room the atmosphere of which is preferably kept at about the boiling point of the solvent. It is stated that the acetylcellulose will solidify upon coming in contact with the hot atmosphere to form a thread which can be drawn or wound without necessitating the use of any precipitant. The solvent laden atmosphere is passed through refrigerating coils and a portion thereby recovered for re-use. Knoll & Co.[3]

1. E.P. 7341, 1903; abst. J.S.C.I. 1904, **23**, 501. F.P. 330714, 1903; abst. J.S.C.I. 1903, **22**, 1100; Mon. Sci. 1904, (4), **60**, 66.

2. E.P. 28733, 1904; abst. J.S.C.I. 1905, **24**, 1299. F.P. 350442, 1904; abst. J.S.C.I. 1906, **25**, 262; Mon. Sci., 1906, (4), **64**, 169. Patentee recommends to use for this process, cellulose acetate obtained according to E.P. 21628, 1901; F.P. 317007, 1901.

3. E.P. 2026, 1907; abst. J.S.C.I. 1908, **27**, 353. F.P. 369123, 1906; abst. J.S.C.I. 1907, **26**, 91; Mon. Sci., 1908, (4), **68**, 28. D.R.P. 180666, 1905; abst. Zts. ang. Chem. 1907, **20**, 1786; Mon. Sci., 1909, (4), **70**, 77; Jahrsb. Chem., 1905-8, II, 982. D.R.P. 180667, 1905, being addition to D.R.P. 180666; abst. Zts. ang. Chem., 1907, **20**, 1786; Mon. Sci., 1909, (4), **70**, 77; Jahrsb. Chem., 1905-8, II, 982.

claim the use of sulfinic acids in the acetation of cellulose intended for filament formation on the assumption that solutions prepared from cellulose thus acetated will keep unimpaired for months and without any loss in viscosity.

The Furst Guido Donnersmarcksche Kunstseiden und Acetatwerke have found[6] a marked advantage in the use of formic acid as a solvent for cellulose acetate intended for filament formation, and have discovered that in the spinning process a thread may be directly produced of sufficient strength when the solution is squirted into an aqueous precipitating bath of suitable character.[7] In point of economy the formic acid process is the equal of others, since the formic acid used may be recovered by the same means as acetic acid. The initial cost at the present price of formic acid is also not unduly high. In order to increase the speed of precipitation or coagulation of the issuing acetate filaments, and to minimize danger of distortion of the filaments before hardening, it has been proposed[8] to add to the solutions before spinning an aqueous precipitating liquid until the acetate is near the coagulating point. Then upon forcing such a solution into water or other fluid in which the cellulose acetate is insoluble, precipitation will occur at once, due to rapid penetration of non-solvent, and such filaments can be drawn off more quickly without breaking, and subsequent sticking together of the formed threads is avoided.[9] H. Dreyfus and

6. U.S.P. 922340, 1909; abst. J.S.C.I. 1909, **28**, 671. F.P. 400652, 1909; abst. J.S.C.I. 1909, **28**, 1061; Mon. Sci., 1910, (4), **73**, 165. D.R.P. 237718, 1907; Zts. ang. Chem., 1911, **24**, 1988; Chem. Zentr., 1911, **82**, II, 922. It. P. 303-136-101262, 1909. For use of lactic acid as solvent see D.R.P. 239701, 1910; abst. C.A. 1912, **6**, 2169.

7. The rapid action is considered to be due to the fact that the skin formed upon the surface of the filament as soon as it enters the precipitating bath is readily penetrated by formic acid and water, so that the coagulating process rapidly extends to the interior of the thread, thus imparting the necessary strength almost at once.

8. Chemische Fabrik von Heyden, E.P. 3973, 1911; abst. J.S.C.I. 1911, **30**, 156; C.A. 1912, **6**, 2172. F.P. 426436, 1911; abst. J.S.C.I. 1911, **30**, 950. Aust. Appl. A-327, Jan. 12, 1911. Belg. P. 232475, 1911. D. R. Anm. C-19868, 1910; C-23158, 1913; C-23487, 1913. In their D.R.P. 273029, 1910, addition to D.R.P. 269193; abst. C.A. 1914, **8**, 2251, 2806, in the manufacture of cellulose acetates the cotton is first thoroughly dried.

L. Schneeberger [10] apply cellulose acetate made according to F. P. 413671, 1910, to the preparation of artificial silk by any of the known processes of manufacture.

K. Hofmann has developed a method of acetate silk formation [11] in which cellulose, oxycellulose or hydrocellulose is converted into a mixed ester by solution in concentrated acetic and phosphoric acids with the aid of sulfuric acid or other stimulant, or if the phosphoric acid is previously heated to 220° so that a portion is converted into pyrophosphoric acid, the use of a catalyst as sulfuric acid becomes unnecessary. If, for example, 20-35 gms. of cellulose are dissolved in a mixture of 30 c.c. concentrated phosphoric acid and 300 c.c. glacial acetic acid at ordinary temperatures, the viscous mass finally obtained can be forced through a capillary orifice into aqueous or alcoholic coagulating solutions and the product washed and dried under tension.

In the foregoing described process the esterized cellulose is directly utilized without precipitation, drying and re-solution, thus introducing a distinct economy. L. Lederer has described this idea more in detail [12] in which he overcomes the injurious effect of the condensing medium and renders superfluous the process of de-acidifying the acetated cellulose by

9. For example, 10 parts of cotton are well kneaded with a mixture of 25 parts of acetic anhydride, 80 parts glacial acetic acid and 1 part pyrosulfuryl chloride. To the clear thick solution thus obtained after about 24 hours, 80 parts of 50% acetic acid are added. The most solid and elastic threads are obtained from such solutions of fatty acid esters of cellulose as contain less fatty acid than the triacetylcellulose. For example, solutions of such acetylcellulose as would split off on saponification 55%-59% of acetic acid give better threads than solutions of triacetylcellulose which on saponification would split off 62.5% acetic acid. In this connection compare Mork, E.P. 20672, 1910; F.P. 416752, 1910.

10. F.P. 413787, 1910; abst. J.S.C.I. 1910, **29**, 1101; Mon. Sci., 1911, (5), **74**, 155.

11. D.R.P. 227198, 1909; abst. J.S.C.I. 1910, **29**, 1300; Chem. Zts. 1910, **9**, 2102; Chem. Zentr., 1910, **81**, [(5), **14**], II, 1349; Jahr. Chem. 1910, 429. See Zeits. Farb. Textind., 1905, **4**, 383; 1907, **6**, 2; Schwalbe, Ber., 1908, **40**, 1347, 4523. In the example given, 300 c.c. concentrated phosphoric acid is mixed with 300 c.c. glacial acetic acid in which 20-25 gm. cellulose is dissolved at the ordinary temperature.

12. E.P. 26502, 1906; abst. J.S.C.I. 1907, **26**, 634. F.P. 371357, 1906; abst. J.S.C.I. 1907, **26**, 340; Mon. Sci., 1908, (4), **68**, 79. Belg. P. 195839, 1906.

precipitation and washing, by adding to the mass after esterification certain basic substances or salts adapted to neutralize the effect of the condensing medium. Among the basic substances found suitable for this purpose may be mentioned methylamine, guanidine, aniline, amidophenols and alkaline formates and acetates.

For example, 100 parts of cellulose are acetylized with a mixture of 500 parts glacial acetic acid, 300 parts acetic anhydride and 10 parts sulfuric acid.[13] When the reaction is completed from 20 to 35 parts of potassium acetate are introduced into the acetylizing mass and carefully mixed by stirring. The patentee claims solutions of cellulose acetate prepared in this manner will keep in good condition for an indefinite period, and surpass the solution obtained from solid acetylcellulose as regards viscosity.

According to the statement of Farbenfabriken vorm. F. Bayer and Co.[14] an exceptional brilliance may be imparted to yarn which has been coated with cellulose esters by filling them with a preparation containing substances capable of softening, swelling or dissolving the coating. Alcohol, acetone, ethyl acetate, acetylene tetrachloride, acetin (acetylated glycerol) and substituted alcohols are specified as being suitable. In their recommended formula, the yarn or textile is treated for some minutes with a mixture composed of 300 gm. of rice starch, mixed with 3000 gms. of water in which 50 gms. of Senegal gum has been incorporated to thicken it. A mixture of 75 gms. of acetin dissolved in 150 gms. of alcohol is next added, and the whole stirred to a homogeneous mass, the starch, of course, remaining insoluble. The thread is treated with this filling, the major portion of which is afterwards removed, and finally dried and polished. The pliability may be increased[15] and a softness imparted by adding to the

13. It is unsafe to use so large proportion of sulfuric acid to cellulose.

14. D.R.P. 240188, 1909; abst. Zts. ang. Chem., 1911, **24**, 2336; Chem. Zentr. 1911, **82**, II, 1563. F.P. 417027, 1910; abst. J.S.C.I. 1910, **29**, 1373; Mon. Sci. 1913, **78**, 20.

15. E.P. 11354, 18193, 1909; 13100, 1910. U.S.P. 1031616, 1912. F.P. 408370, 1910, and First Addition No. 12469, and Second Addition of June 11, 1910, thereto. Aust. P. 29b, 1642, June

mixture certain substituted organic amins, anilids, imids, organic ethers and esters, as specified under the topic "Baykogarne."

L. Lilienfeld [16] produces impressions fast to water on textile materials by combining with cellulose acetate, organic acid esters of high boiling point, the esters of phthalic acid being specified as especially suitable in this respect. For example, 100 parts of cellulose acetate is dissolved in a suitable solvent together with 50-150 parts of ethyl phthalate,[17] the solution being applied as a dressing composition to the textile fabric either before or after the goffering process. This method is stated to be most applicable for imparting resistance to water to those impressions on textile fabrics particularly known as "silk finish," fabrics so dressed or coated preserving their softness to the touch when sufficient quantities of the combinations are applied. The high capacity for resisting water is best shown upon those designs applied by means of silk-finishing or goffering rolls; glue or gelatin may also be combined with the acetyl-cellulose as a pigment vehicle or carrier.

F. Sammet [18] produces filaments and films from cellulose formate, by dissolving in 98% formic acid to a 20% solution.

A. Stiebel [19] prepares iridescent filaments and films by means of an intermediate film composed of bismuth oxychloride (bismuth subchloride) or bismuth subnitrate with cellulose acetate or nitrate, the cellulose ester serving as the carrying medium for the basic bismuth salt.

21, 1909. Abst. J.S.C.I. 1910, **29**, 533, 575, 624, 752, 1299, 1371; 1912, **31**, 770. See W. Vieweg, "Manufacture of Acetate Silks"; E.P. 15544, 1914; D. R. Anm. June 28, 1913.

16. U.S.P. 904269, 1908; abst. J.S.C.I. 1908, **27**, 1202. E.P. 4597, 1906; abst. J.S.C.I. 1907, **26**, 146. D.R.P. 175664, 1903; abst. Zts. ang. Chem., 1907, **20**, 461. U.S.P. 888516, 1908; abst. J.S.C.I. 1908, **27**, 683. E.P. 592, 1907; abst. J.S.C.I. 1908, **27**, 73. D.R.P. 169782, 1904. D.R.P. 182773, 1904; abst. Zts. ang. Chem., 1907, **20**, 2090. Wagn. Jahr. 1907, II, 463. E.P. 14483, 1903.

17. Suitable solvents are methyl alcohol, acetone, ethyl alcohol alone or mixed with acetic anhydride, ethyl acetate, butyl acetate or amyl acetate.

18. D. R. Anm. S-37509, 1912; abst. Zts. ang. Chem. 1913, **26**, 700.

19. D.R.P. 231030, and Addition thereto, D.R.P. 267370, 1913; abst. C.A. 1912, **6**, 1717; 1914, **8**, 1711.

Bayko Yarn. The Farbenfabriken vorm. F. Bayer and Co. have placed upon the market under the above name a product which consists of dyed or undyed cotton or other vegetable, animal or metallic filament which has been covered with finely powdered metals, the attachment of the metal to the filament being by means of a solution of cellulose acetate. The preparation of gold and silver yarns, both the so-called genuine and the imitation, is a somewhat difficult class of work, calling both for trained and expensive labor, and the provision of specially constructed machines. The method ordinarily in use consists in mechanically twisting the metallic film around the spun yarn or fine metal core, and in addition to the difficulty of producing regular results, there is a large loss of waste, which materially increases the cost of the finished yarn. There is also the drawback of the difficulty of producing a firm adhesion between the metal and the thread, lustrous threads prepared in this manner suffering from lack of durability.

In producing Bayko yarn, threads spun from cotton, flax, wool, silk or metallic threads, wires or bands are passed through a mixture of metallic bronzes or powders with solutions of cellulose acetates, with or without the addition of other suitable pigments to insure a homogeneous mixture of the bronzes with the solutions. The threads on emerging from this mixture may be passed through a further solution of cellulose acetate to protect the particles of bronze from the sulfur and oxidizing influences in the atmosphere, or they may be finished by calendering, polishing, pressing, softening, filling or homogenizing.

1. D.R.P. 243068, 1909; F.P. 408370, 1909; abst. J.S.C.I. 1910, **29**, 624. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. U.S.P. 1031616, 1912; abst. J.S.C.I. 1912, **31**, 770. Chem. Abst. 1912, **6**, 2687. Belg. P. 220225, 1909. Swiss P. 48975. Aust. P. 29b, 4642, 1909. The U. S. Patent was taken out in the name of P. Benrath, E. Damm and O. Stephani. The metal powder or pigments are said not to penetrate the core of the thread to any appreciable extent, but remain largely as a superficial layer of discrete metallic particles or flakes, each incased by and incorporated with the acetylcellulose. For "Manufacture of Artificial Silk Threads from Cellulose Esters," by J. Duchaux, see Belg. P. 245532, 1912. For articles on "Baykogarne," see Prom. 1911, **7**, 9. Konfecktionaer, 1911, No. 16. S. Feitler, "Das Celluloid und Seine Ersatzstoffe, 1912; 43-45.

As an example of the method of yarn formation, a cotton thread is slowly drawn through a chloroform solution containing 5% of acetylized cellulose [2] and carrying 15% of gold-bronze in suspension. The thread on emerging from the chloroform is passed through dry chambers to evaporate off the cellulose acetate solvent, and then spooled. Or, a thread may be drawn through a 10% solution of cellulose acetate in acetone [3] carrying 30% of copper-bronze in suspension. The thread upon emerging from the solution may be dried as before, then passed through a cellulose acetate solution carrying no pigment, dried and reeled. Where wire is to be coated, it may be desirable to first coat the wire with fine tissue paper, which may or may not have been dyed before coating, it being claimed that the adhesion of the coating to the metal is materially increased in this way.[4]

It has been found that the softness of threads prepared in this manner may be considerably enhanced by adding to the cellulose acetate and bronze coating solutions certain substances which by their action impart softness to the coating. Especially valuable in this connection are substituted organic amines, anilids, amids, imids, organic ethers, esters, and halogen substituted ammonias, such as ethyl-*o*-toluidine, methylacetyl-*o*-toluidine, acetylbenzoyl-*o*-toluidine, ethylbenzoyl-*o*-toluidine, diethyldiphenylurea, acetanilid, methylbenzoyltrichloranilid, phthalimid, *b*-naphthyl acetate, benzylidendiacetoacetic ester, phenoxy acetic ester, phthalic acid esters, oxalic acid esters, triphenyl phosphate, triphenyl borate, acetin, triacetin, pentachlorethane, acetylene tetrachloride, dichlorhydrin, acetodichlorhydrin and chloral hydrate. For

2. Preferably prepared according to U.S.P. 790565, 1905; F.P. 317007, 1901; D.R.P. 150825, 159524, 1901; E.P. 21628, 1901. For mechanical appliance to coat yarns with cellulose acetate, see Bayer & Co., D.R.P. 227238, 1909.

3. Preferably prepared according to E.P. 24067, 1906; U.S.P. 838350, 1906; F.P. 371447, 1906.

4. E.P. 18193, 1909; abst. J.S.C.I. 1910, **29**, 575. First Addition No. 12469, 1910, to F.P. 408370, 1909; abst. J.S.C.I. 1910, **29**, 1299. D.R.P. 248946, 1909, being Addition to D.R.P. 243068, 1909; abst. Wag. Jahr. 1912, II, 502. D.R.P. cites D.R.P. 150825, 1904; abst Zts. ang. Chem., 1904, **17**, 1123, of A. Forster in which nitrocellulose solution containing a small amount of water is used for the same purpose as above.

instance, if a cotton thread is slowly drawn through 100 parts of a 10% chloroformic solution of cellulose acetate to which 3 parts of ethylbenzoyl-*o*-toluidine has been added, the addition of 15 parts of gold bronze will not overcome the softness induced by the presence of the amid.

The product of this process is intended for the manufacture of embroideries, tulle, veilings for the trimming of hats and costumes, and the tieing of flowers, and may conceiveably have a large and varied field of application. There is the advantage that the finished yarn is waterproof and difficultly flammable due to the presence of the cellulose acetate. By dyeing the yarn certain colors variegated effects are produced. A yarn dyed blue when coated with a pure yellow bronze gives a fluorescent and dichroic effect of all shades of green from yellow to blue, while in a similar manner various tints of orange may be prepared by superposing a yellow bronze upon a thread dyed red. It is apparent that an endless variety of shades and combinations is possible in this manner. Where the metallized yarn is given a second coat of cellulose acetate to further fix the bronze, this operation, aside from affording protection to the metal against the oxidizing influences of the atmosphere, admits of further effects being produced by dyeing the solution various shades which either harmonize or contrast with the color of the bronze, or the shade of the core of thread upon which the bronze was deposited.

This form of metallized yarn has been studied by several,[5] more recently and completely by A. Herzog.[6] The bakyo yarn examined by Herzog consisted of a core either of cotton or tussah silk, the cotton center being of double-twist and the tussah silk being used where great fineness of denier was desired and especial firmness with regard to tearing as in the manufacture of tulle. The cotton thread examined averaged 95 filaments, but this would vary considerably according to

4.5. E.P. 13100, 1910; abst. J.S.C.I. 1911, **30**, 533. Second Addition dated June 11, 1910, to F.P. 408370, 1910; abst. J.S.C.I. 1910, **29**, 1371.

5. Confectionair, 1911, No. 16. Prometheus, 1911, No. 1145.

6. Kunst. 1912, **2**, 104-109; abst. Chem. Abst. 1912, **6**, 2320.

the count and number of the thread used. Mercerized or lustered cotton possesses certain advantages where extreme softness is desired. The optical behavior of the acetylcellulose cementing portion on the yarn examined was essentially different from acetate silk and horsehair filaments. He found the average cross section of a single filament to be 0.0372 sq. mm., or 100%; same for the nucleus filament 0.0239 sq. mm., or 64.2%, and for the envelope 0.0133 sq. mm., or 35.8%. Metric yarn number 29.6 with a weight of 33.8 gms. per 1000 meters. Thickness of filament, minimum, 0.162 mm., average, 0.191 mm., and maximum, 0.266 mm.; a lack of uniformity in the thickness of 5.7%. Tensile strength, minimum, 410 gms., average 462 gms., the lack in uniformity in strength being 4.8%. Limit of ductility, 13.7 km.; elongation minimum, 4.6%, average 4.9%, maximum, 5.2%. The apparent specific gravity, calculated from the yarn number and the average thickness, is 1.18.

In the printing of fabrics and the production of brocaded and crush effects, cellulose acetate solutions with metals and finely divided pigments offers another wide field. The pigment or bronze is mixed with the cellulose acetate solution containing solvents of low volatility as acetin, resorcinol diacetate, oil of cloves, the glycol diacetates, or cinnamic aldehyde, and printed on the fabric with pressure. After drying a permanent colored pattern results, which is waterproof and will stand considerable rubbing. It is claimed that metal-coated yarns and printed piece goods may be produced by this process at two-thirds the cost of the customary methods.

L. Lilienfield in a series of patents[1] has described the preparation of textile finishes by incorporating finely ground

1. U.S.P. 904269, 1908; abst. J.S.C.I. 1908, **27**, 1202. E.P. 4597, 1906; abst. J.S.C.I. 1907, **26**, 146. D.R.P. 175664, 1903; abst. Zts. ang. Chem., 1907, **20**, 461. U.S.P. 888516, 1908; abst. J.S.C.I. 1908, **27**, 683. E.P. 592, 1907; abst. J.S.C.I. 1908, **27**, 73. D.R.P. 169782, 1904. D.R.P. 182773, 1904; abst. Zts. ang. Chem. 1907, **20**, 2090. E.P. 14483, 1903; abst. J.S.C.I. 1903, **22**, 1345. U.S.P. 904269, E.P. 4597, 1906, D.R.P. 175664 are the same. U.S.P. 888516, E.P. 592, 1907, are the same. To increase the flexibility of the acetate-mica combination, ethyl phthalate (U.S.P. 888516) or ethyl palmitate or acetylpalmitic esters (U.S.P. 904269) may be added. See Lehne's Farb. Ztg., 1898, 190.

mica, bronzes and pigments with cellulose acetate and other cellulose esters, subsequently printing on this acetate lacquer compound. The object of mica is to accentuate the glossy effect obtained by means of the cellulose acetate lacquer upon drying, the effect being further heightened by printing upon the fabric with rollers having a rippled or other irregular surface. After printing the preparation is dried and then finished on ordinary finishing calendars. The effect of the pattern produced is not impaired by dampness due to the water-resisting properties of cellulose acetate, the method thus being applicable for book-binding, card decoration, wall-papers, lace, embroidery, trimmings and artificial flower manufacture.

Artificial Horsehair. The manufacture of so-called artificial horsehair which may be carried out by such general processes as are described in DRP 123309 or DRP 129420, are based upon the production of a homogeneous thread which in one case is formed by allowing a plurality of artificial silk threads to run together immediately after their formation, and in the other case by softening or dissolving separate threads by the employment of suitable solvents, after which they are united into a filament of larger diameter. In certain instances, however, it is desirable to produce a stronger thread of great elasticity and springiness without the necessity for the material to be homogeneous. Such a product may be obtained [1] if two or more ready-formed threads of cotton, ramie, nitrocellulose or artificial silk are drawn as single threads (twisted or untwisted) through a solution of cellulose acetate, thereby causing the separate filaments to adhere together in the formation of a water-repellant single thread by precipitation of the acetate in a suitable coagulating bath. The fusion in this manner of separate filaments into a single thread is accompanied by no loss in tensile strength while insulating properties are obtained peculiar to cellulose acetate. Alcohol is claimed as preferable as the precipitant.

The Vereinigte Kunstseidenfabriken [2] take the waste of

1. Furst Guido Donnersmarck'sche Kunstseiden und Acetatwerke, E.P. 23688, 1906, application for this patent being void.
2. D.R.P. 181784, 1905.

artificial filaments, first untwist the material and then bind the filaments together by saturation with cellulose acetate solution, followed by drying under slight tension.

Microscopy of Acetate Silk. The microscopy of cellulose acetate filaments has been investigated by W. Massot,[1] and more recently considerably extended by A. Herzog.[2]

1. Microscopic behavior. Examined microscopically the individual filaments are uniformly cylindrical, with only occasional flat broadenings. The average diameters of the individual fibers as the mean of 100 measurements in water is 42.3 microns, with a variation of about 2.9%, the average area of the cross section being 0.001234 sq. mm. With the exception of gelatin silk, no other class of artificial filaments show such regularity and uniformity. Immersion in water distinguishes acetate silk from all others, on account of the absence of any marked swelling. Cross sections of the filaments appear oval or cylindrical with relatively larger indentations. The irregular rectangular sections are few, which obviously correspond with the above-mentioned flattenings. The more recent acetate silk differs essentially from the older acetate threads in their external form, the latter being more like collodion.

2. Ultramicroscopic behavior. With the ultramicroscope, acetate and collodion silk are indistinguishable. In either case there appears faintly luminous reticulated structures distorted by more or less frequent impurities, the meshes of the network being elongated. In the older acetate silk many solid impurities are observable and shown by their strong double refraction between crossed nicols (polarized).

3. Specific gravity. By means of a picnometer and using petroleum as the immersion fluid, the sp. gr. was found to be 1.25. According to Hassack[4] and Saget and Suevern,[5]

1. Farb. Ztg. 1909, **18**, 146, 166, 182; abst. Zts. ang. Chem. 1909, **22**, 241, 252, 299, 305; Chem. Zentr. 1909, I, 801; Bull Soc. Chim., 1909, (4), **6**, 555.

2. Zts. ang. Chem. 1906, **19**, 1899; Oest. Chem. Ztg. 1906, **9**, 166; Jahr. Chem. 1905-8, II, 4624; Chem. Centr. 1906, **77**, II, 372.

4. See C. Hassack, Oest. Chem. Ztg. 1900, **3**, 235, 267, 297; abst. Chem. Centr. 1900, I, 1312; II, 226, 359; Zts. ang. Chem. 1900, **13**, 89.

5. Bull. Soc. d'Encouragement, 1906, 540.

natural silk has a sp. gr. of 1.36, artificial silk from cellulose 1.50-1.53, from which it appears that acetate silk has the lowest specific gravity.

4. Firmness and elasticity. By the use of a Schoppers machine with hydraulic power the breaking strain of a fiber of 18 air dry filaments gave 226.25 gms. as the mean of fifty determinations. Acetate fibers gave when damp a breaking strain of but 43.3% when tested by Herzog, or an absolute breaking strain per 1 cu. mm. sectional surface of 10220 gm. for the dry and 5800 gm. when damp.[6]

The elasticity (expansion) of acetate silk amounts wet and dry to 17%.

5. Microchemical reactions. Acetate silk tested with the reagents used in the technical microscopy of silks give the following results: Iodine and sulfuric acid (v. Hoehnels paper reagent), yellow color; zinc chloride and iodine, yellow; soluble slowly in cold concentrated sulfuric acid, more easily soluble in cold glacial acetic acid; half-saturated chromic acid produces moderate swelling without solution; ammoniocupric oxide causes slight swelling without solution; ammonionickel oxide acts the same; alkaline-copper glycerol is without action. Acetate silk may also be identified by the following simple test: If a bundle of fibers be ignited, similar phenomena appear as with animal fibers, but the gases do not smell of nitrogen (burnt hair). To distinguish between acetate silk and denitrated nitrocellulose, viscose or cuprammonia filaments, add acetone or chloroform or tetrachlorethane and alcohol. Acetate filaments will pass into solution while other filaments are unaffected. Not denitrated nitrocellulose filaments are recognized by their inflammability and solubility in cold amyl acetate.

6. Optical properties. Acetate silk is but feebly doubly refractive, in which respect it stands between the still weaker refracting gelatin silk[7] and the stronger refractive cellulose

6. The experiments of Hassack shows that acetate silk has the greatest strength when wet of all artificial silks.

1. A. Herzog, Oest. Chem. Ztg. 1906, No. 12. According to F. Beltzer, Mon. Sci. 1911, (5), 75, 641, acetylcellulose threads are generally regular and cylindrical without longitudinal stripes and

silks. Between crossed nicols polarization colors appear, which move from dark to greyish blue of the first order. In the parallel position, slightly marked, mostly yellowish brown tones appear. If between the crossed nicols a retarding quartz plate is placed, definite results are obtained.[8]

Acetate silk dyed with Congo red or other similar dyestuffs used for testing, give no dichroism.[9] In this respect therefore it differs from all other artificial silks except gelatin (which technically is valueless).

7. Refractive power. The refractive coefficient of both the older (chloroform soluble) and newer (acetone soluble) acetate silks is exceptionally low. Massot states that acetate silk becomes practically transparent when mounted in glycerol, and therefore nearly indistinguishable. Herzog has found that the refractive indices in the longitudinal view of the filaments vary but slightly from one another, and approximate 1.4740 to 1.4790, measured for the sodium (D) lines.[10] The

without excoriations. The walls of the fibers are smooth, while occasionally the presence of a narrow and nearly invisible central tube can be observed. The diameters vary between rather wide limits, from 0.03-0.06 mm. Iodine dissolved in potassium iodide gives irregular coloring, varying from yellow to brown, even with one fiber only. Potassium permanganate colors red to brown. Ruthenium red gives irregular dyeings. Alkali swells the fibers, and then if ruthenium reagent is added, the color remains unchanged. Methylene blue 2B, crystal green and congo red give irregular colorings. A characteristic reaction, therefore, of acetate silks is their irregularity in dyeing. Acetate silk may also be recognized by the pronounced odor of acetic acid when incinerated.

8. A. Herzog, Chem. Ztg. 1910, **34**, 347; abst. J.S.C.I. 1910, **29**, 555; C.A. 1910, **4**, 2371, found that the longer axis of active elasticity ellipse (edge and surface parts of the fiber) is at right angles to the longitudinal length of the fibers. This behavior is in marked opposition to that of all other artificial silks, and is sufficiently characteristic to admit of ready differentiation of acetate silk from all other artificial silks.

9. See A. Herzog, Zeit. Farb. Text. Ind. 1904, No. 14.

10. These observations stand in accord with the low specific double refraction, which is demonstrated by the relatively coarse fibers by low polarisation colors. In the mean refraction acetate silk coincides approximately with oil of lemon $(n)_D=1.4786$, $t=17$ degrees. Consequently fibers imbedded in oil of lemon disappear almost completely (microscopically controlled). Since the visibility of an undyed fiber depends under microscopic examination almost exclusively on the difference of its mean refractive index and that of the imbedding fluid, Massot's observation above mentioned is readily understood. Glycerine comes very close as regards

two principal refractive coefficients (or indices) vary but little,

refractive index to acetate silk, whilst the other artificial silks are considerably more refractive and therefore stand out in glycerine much more distinctly from the background.

In a subsequent investigation (Kunst. 1913, **8**, 148, 170; abst. C.A. 1913, **7**, 2470) it was found that acetylcellulose filaments show only feeble double refraction, which may be shown in the polarization microscope, according to the optical thickness of the objet, by the appearancce of lower polarization colors (first order). With a gypsum plate (red I) it is shown that the character of the interference colors varies significantly from that of all other artificial silks and horse-hair substitutes. After keeping 2 years in Canada balsam, and in air, striking changes in light-refraction power and internal structure could be noted. The optical changes which the filaments gradually undergo are so great that in many cases only the outer parts retain their original character. The change between altered and unaltered places is abrupt; frequently the altered parts with numerous sinuosities project into the outer filament mantle (zone). A yellowish to brownish coloration goes hand in hand with the change in refractive power. It is concluded that the following conditions govern the changes: (1) The nature of the esterification process in the manufacture of the acetylcellulose; (2) the spinning process and especially the nature and time effect of the precipitating bath used; (3) reeling and drying process; (4) the action of the different incompletely removed substances formed in the precipitating bath upon the finished filament; (5) the nature of the including medium (Canada balsam, water, air, etc.); (6) spontaneous chemical decomposition of the acetylcellulose esters. The changes that acetate filaments undergo with time are accompanied by loss in strength. *Behavior on stretching*: Acetate filaments on pulling react in the beginning very rapidly and in same manner as filaments of glass, gelatin, etc. Such observations using a retarding gypsum plate (best red I) show readily the change in the height and character of the interference colors; a slight pull on a filament (placed in the microscope) suffices to cause a significant elevation of the interference colors. The same is true for bending: the convexes produce an elevation similar to that from a pull; the concaves, a striking lowering of the original polarization color. All acetylcellulose filaments are directly in the zone of their greatest extensibility almost optically indifferent; a series of observations with the polarization microscope and the Schopper strength tester are reported in detail showing this optical indifference, together with explanation for same. *Influence of water and other liquids upon the mechanical and optical properties*: Acetylcellulose filaments are unfavorably influenced by water, even at ordinary temperature. This is true for acetate silk as well as the coarse horse-hair-like filaments. The diminution of strength is essentially greater with fine than with coarse filaments; the average loss of strength through moistening is: for artificial silk from acetylcellulose, 45%; for horse-hair-like material, 23%. It is concluded from a series of experiments on dry and moist heating that: (1) Heating exerts in both dry and moist condition an unfavorable influence upon the tensile strength and stretch of acetate filaments. Heating with water at 100° is an exception, increasing the strength. (2) Dry heat acts in all cases more unfavorably than moist. (3) Strength decreases

while in general the fibers coincide in their mean refractive index with oil of lemon, in which consequently they become almost invisible.

Strengthening Artificial Filaments. As is well known, articles made from denitrated nitrocellulose, cuprammonia or viscose suffer in the natural state from lack of rigidity. It has been proposed to overcome this [1] by applying to such articles in the form of hat trimmings, lace, passamenterie, and embroidery, a solution of cellulose ester as the acetate in sufficient thickness to impart the desired rigidity and impermeability without at the same time noticeably detracting from their luster. A 10% solution of cellulose acetate in tetrachlorethane and acetone with or without the addition of a small amount of castor oil should be suitable for the purpose. If the fabric is colored, the acetate lacquer may be dyed the desired shade before application, thus making the coating practically inconspicuous.

Artificial Sponge. In the preparation of artificial sponge according to the process of V. Ottorepetz,[1] a concentrated

rapidly with increasing temperature. (4) The break on stretching is unfavorably influenced throughout by warming; dry heating is more injurious here than the moist. Especially striking is the loss of ductility in the moist filaments before breaking. (5) The external form of the filaments is apparently unaltered by dry heat, but on moist heating even at 110° significant deformations are to be observed, as an irregular, vesicular relief on the external filament part; the filaments swell considerably and become opaque and milky looking. The opacity is due to the intercalation of numerous needle-like crystals, whose long axis is parallel to the filament direction. The chemical nature of these crystals is yet to be determined. (6) Dry heating produces at 100° a decided yellow coloration, which becomes at higher temperatures brown and black. Moist heating does not change the color appreciably; only at temperatures of 150° is a noticeable brown coloring to be observed. Treatment of acetate filaments with different organic and inorganic substances causes swelling, with structure changes in part. In the cold a decided influence of the character of the interference colors is to be observed. Cuproammonium does not alter the optical relations of the filaments at all; dilute and concentrated alcohol exert such a changing effect that nothing definite could be determined. The filaments on heating in the air undergo optical changes, that remain fixed in great part on cooling.

1. Compagnie Francaise des Applications de la Cellulose, F.P. 417599, 1910; abst. J.S.C.I. 1911, 30, 19. The sthenosage of artificial filaments with aldehydes is not as applicable to acetate filaments.

1. E.P. 23196, 1913; abst. J.S.C.I. 1914, 33, 858. E.P. 21524, 1914.

solution of a derivative of cellulose, such as the nitrate, acetate or viscose, is mixed with such fibrous material as cotton, and a readily soluble substance such as a salt or sugar. The paste thus obtained is immersed in water or a dilute acid or salt solution, so that pores are formed in the mass owing to the solution of the salts, the cellulose derivative remaining in the form of a spongy body enclosing the fibrous substance.

In another process [2] a mixture of concentrated solution of cellulose derivative as cellulose acetate, fibrous material and some water-soluble material as sugar or salt is made, the paste being placed in water, dilute acids or saline solutions. The salt or sugar is said to form pores in the mass, the cellulose material precipitating around the fibrous material, imparting to the mass the appearance and properties of the sponge.

The Akt. Ges. fuer Anilin Fabrikation [3] prepare artificial rubber by mixing acetylcellulose and a difficultly volatile material imparting plasticity, the product being suitable for imitation leather if pressed.

Dyeing Cellulose Acetate. The acetylated celluloses possess but little affinity for dyestuffs, especially for the direct or substantive colors, in which respect they differ materially from cotton or silk. Wagner has taken advantage of this fact in the use of acetylcellulose filaments in conjunction with natural cellulose and silk, where it is desired to impart differential coloring in the weft or weave. By associating, for instance, cellulose acetate filaments with natural silk according to definite patterns, the finished fabric may be dyed so as to show colorless and colored fibers. Those direct dyeing dyestuffs are selected which possess the least affinity for the

2. P. Roeder & B. Raabe Akt. Ges., F.P. 463498, 1913; C.A. 1914, 8, 3225. P. Roeder and B. Raabe, Aus. Ad. 8607, 1913, to Aus. P. 63556; abst. C. A. 1914, 8, 3354.

3. F.P. 463622, 1913; abst. C.A. 1914, 8, 3245. See their Aus. Appl. 8334 of 1911. According to a recent statement (E.P. 1156, 1914; Add. to E.P. 10706, 1912; abst. Kunst. 1914, 4, 310) this firm prepares a superior acetylated cellulose for technical uses by treating cellulose with 10-30 parts of 68-70% nitric acid for one-half hour, after which to 10 k. original cellulose is added 30 k. acetic anhydride and 40 k. glacial acetic acid together with 600 gms. of bromine, the reaction being carried on at 30-50° until the stage of desired solubility is reached, when the esterized cellulose is precipitated by water and washed in the usual manner.

cellulose acetates, the fabric being immersed in the dyebath at a moderate temperature, sodium chloride or sodium phosphate being used to assist in depositing the color on the natural fiber. The acetates differ markedly from the nitric esters in that filaments of the former may be subjected to much longer immersion in the dyebath and at considerably higher temperatures without appreciably tendering.

It has been found [1] that while water or alcohol separately exert but little influence in assisting the penetration of dyestuffs in cellulose acetate filaments, if the two be combined, dark tints of many colors are readily obtainable. For instance, from an aqueous solution of methylene blue, cellulose acetate filaments cannot be dyed at all, while an alcoholic solution of the same dyestuff produces feeble tints. On the other hand, full shades are obtainable from a bath containing equal volumes of both. Similar typical results are stated to occur with such dyestuffs as rhodamine, erica, chrysoidine, naphthol-yellow, or fuchsine (magenta). As a second solvent in addition to water may be mentioned methyl alcohol, acetone, or acetic acid.[2] This generalization does not always hold good.

1. Actien-Gesellschaft f. Anilin-Fabrikation, D.R.P. 193135, 1905; abst. Chem. Zts., 1908, 7, 630; Wagn. Jahr .1907, II, 433; Zts. ang. Chem., 1903, 21, 1266; Mon. Sci., 1910, (4), 78, 158. E.P. 1939, 1906; abst. J.S.C.I. 1906, 25, 1216. F.P. 362721, 1906; abst. J.S.C.I. 1906, 25, 692.

2. The invention is illustrated by the following examples, the parts being by weight:

(1). Two parts of methylene blue are dissolved in a mixture of 200 parts of water and 150 parts of alcohol, this solution forming the dyebath for 19 parts of cellulose acetate which is immersed at the ordinary temperature for about a quarter of an hour. Either methyl or ethyl alcohol may be used.

(2). Two parts of magenta (fuchsin) are dissolved in a mixture of 500 parts each of water and glacial acetic acid, in which solution are dyed 20 parts of acetylated cellulose for 20 minutes at room temperature. In this way there is obtained a deep red shade, whereas from an aqueous magenta solution acetylated cellulose is not dyed at all.

(3). A solution of 10 parts of naphthol yellow S (an acid dyestuff) is prepared in a mixture of one-half liter each water and alcohol, 20 parts of cellulose acetate being introduced at 70° C, and carefully treated at this temperature for one hour. The material is then washed in warm water, pressed and dried at a temperature of 80-100°, a fine yellow color being produced.

(4). 10 parts of erica B. (a substantive cotton dyestuff) are dissolved in a mixture of 500 parts of water and 500 parts of

Knoll & Co. have found [1] that the absorptive power of dyestuffs is materially increased if the acetate is soaked for some time in a fluid capable of modifying the cellulose acetate by swelling, inflating or otherwise increasing the porosity of the fibers. The process consists in treating the filament or other product of cellulose acetate at ordinary or elevated tempera-

alcohol, either methyl or ethyl. In this dyebath 20 parts of cellulose acetate are treated at ordinary or slightly elevated temperatures, and continued until the desired depth of shade is obtained.

(5). Ten parts of ponceau 4 GB (an acid azo dyestuff) dissolved in a mixture of 500 parts each of alcohol and water produces a deep orange yellow shade, the depth of coloring depending upon the elevation of the temperature of the dyebath and the length of time of immersion.

(6). A deep orange may be obtained by the use of chrysoidine (a basic dyestuff), 20 parts of acetylated cellulose being treated with a 0.2% solution in equal weights of acetone and water. The various acetylated celluloses, especially those which have undergone partial hydration, require alterations in the conditions of dyeing as specified in the above examples.

1. U.S.P. 961241, 979966, 1910, 981574, 1002408, 1911; abst. J.S.C.I. 1910, **29**, 876; 1911, **30**, 126, 206, 1157; Mon. Sci., 1910, (4), **73**, 135. E.P. 24284, 1907; abst. J.S.C.I. 1908, **27**, 1150; Mon. Sci., 1911, (5), **74**, 92. E.P. 7743, 1909; abst. J.S.C.I. 1910, **29**, 209. F.P. 383636, 1907, and First Addition thereto dated Apr. 5, 1909; abst. J.S.C.I. 1908, **27**, 332; 1909, **28**, 1199. D.R.P. 198008, 1907; abst. Chem. Zts., 1908, **7**, 865; Zts. ang. Chem., 1908, **21**, 1471; Wagn. Jahr. 1908, II, 409; Bull. Soc. Chim., 1909, (4), **6**, 557. D.R.P. 199559, 1907; abst. Chem. Zentr. 1908, **79**, 271; Zts. ang. Chem. 1908, **21**, 1810; Bull. Soc. Chim. 1909, (4), **6**, 557. D.R.P. 234028, 1908; abst. Zts. ang. Chem. 1911, **24**, 1151.

The relation of this important series of patents to each other is as follows: E.P. 24284, 1907; F.P. 383636, 1907; U.S.P. 961241, 1910; U.S.P. 979966, 1910; U.S.P. 1002408, 1911; D.R.P. 198008, 1907, 199599, 1907, are the same. D.R.P. 199599, 1907; U.S.P. 961241, 1910, are the same. E.P. 7743, 1909; U.S.P. 981574, 1911; First Add. F.P. 383636, 1909; D.R.P. 234028, are the same.

(1). U.S.P. 961241, D.R.P. 199559, cover swelling the cellulose acetate to increase receptiveness to dyestuff.

(2). U.S.P. 979966 covers impregnation with *b*-naphthol and *p*-aminophenol.

(3). U.S.P. 1002408 covers impregnation with *p*-nitranilin, aminoazobenzene, *a*-naphthylamin, *b*-naphthylamin, benzidin, dianisidin, *m*-phenylenediamin, *p*-aminophenol, and napthionic acid.

(4). D.R.P. covers (2) ad (3) above.

(5). E.P. 24284, 1907; F.P. 383636, each cover (1), (2), (3) above. E.P. 7743, 1909; First Addition to F.P. 383636; D.R.P. 234028 and U.S.P. 981574 cover treating acetylcellulose with hydrochloric acid to enhance its capacity for dye absorption. D.R.P. 234028 cites D.R.P. 199559, 198008. E.P. 7743, 1909, cites E.P. 24284, 1907. U.S.P. 961241 cites D.R.P. 193135. The United States patents are taken out in the name of E. Knoevenagel.

tures until the fiber or fabric has been expanded to the required porosity, in which condition it is introduced into the dyebath and treated in a similar manner to the dyeing of cotton with direct dyestuffs. Fifty per cent. aqueous alcohol or dilute acetic acid at ordinary temperature for twelve hours gives sufficient expansion for ordinary depth of shade. Substances which, like ether or aniline, are substantially insoluble in water, also produce good results, provided the cellulose acetate is allowed to remain in the liquids of their solutions for a considerable length of time. Soap solutions, especially when warm, although acting in the same direction, are more feeble than dilute alcohols.

This process affords the advantage that the actual dyeing may be performed in aqueous solution the same as for acid, basic or vat dyestuffs, so that for dyeing varied classes of dyestuffs, one kind of bath only is required, i. e., dilute alcohol. In this bath the acetylcellulose is allowed to remain with gentle handling for the required time, the aqueous alcohol carefully removed by wringing, treated with a softening solution if desired, and dried at a low temperature in a loose condition.

The swelling or modification of the surface of cellulose acetate in order to increase their receptiveness to dyestuffs, may be produced by inorganic acids as well as by organic compounds.[1] Not only is the swelling accompanied by a large increase in the power of absorption for dyes in dyeing, but likewise the power of absorbing phenols and amins is enhanced, so that these bodies may be attached to the cellulose acetate and then converted into dyes on the fiber by known methods.[2] In this manner impregnation with *b*-naph-

1. U.S.P. 961241, 1910; F.P. 383636, 1907. Methylene blue, malachite green, fuchsin and saffranin are particularly recommended among the basic dyestuffs, although auramine, rhoduline heliotrope, methyl violet, induline and the basic nigrosines are satisfactory.

2. The process is illustrated by the following example: Cellulose acetate films or filaments are treated with concentrated aqueous hydrochloric acid, preferably of about 37% strength, or a similarly acting acid of suitable strength such as 65% hydrobromic acid, 50% nitric acid or 50% sulfuric acid, for about 5 minutes, thereby causing the acetate to swell and increase in volume. The acetate is washed and before drying is immersed in the dyebath. Amines and phenols

thol,[1] *p*-aminophenol,[2] anilin,[3], *p*-nitranilin,[4] aminoazobenzene,[5] *b*-naphthylamin,[6] benzidin,[7] dianisidin,[8] *m*-phenylenediamine,[9] *p*-aminophenol [10] or napthionic acid [11] lead to a series

(for example aniline and *b*-naphthol), are readily absorbed after the cellulose acetate has been inflated by the acid treatment.

1. U.S.P. 979966. Cellulose acetate filaments impregnated for half an hour at a temperature of a water bath in 0.5% solution of *b*-naphthol and rinsed with water give nitranilin red when coupled with 1.5% *p*-nitranilin hydrochloride solution which has been diazotized in the usual manner with acidified solium nitrite solution. Or, by treating the filaments with *a*-naphthylamine instead of *p*-nitraniline hydrochloride, *a*-naphthylamin bordeaux is produced.

2. By impregnation of cellulose acetate with 9.5% solution of *p*-aminophenol at water bath temperature for about 10 minutes, then diazotizing and developing with alkaline pyrogallol solution, azochromin is produced.

3. By impregnating cellulose acetate filaments at the ordinary temperature for about 3 hours in a 2% aqueous solution of aniline, rinsed in water and diazotized in the usual manner with 2% nitrite in cold water with 4-5% sulfuric acid for about 3 minutes, aniline yellow results by treating the fibers with aniline. If the aniline be substituted by 1-2% *b*-naphthol sodium solution (*b*-naphthol rendered soluble in water by treatment with NaOH) Soudan I is deposited on the fiber. To produce aniline black, the diazotized acetate filaments are treated with 1.4 parts potassium bichromate and 1.4 parts of concentrated hydrochloric acid in 40 parts of water, and after covering the filaments with this solution for about a quarter of an hour at ordinary temperatures, heating finally to 80° for about a minute develops the black.

4. Filaments brought at the temperature of the waterbath for half an hour into a 4% aqueous *p*-nitranilin solution, briefly rinsed and then diazotized, develop nitranilin red when subsequently treated with *b*-naphthol.

5. When acetate filaments are impregnated for about 10 minutes with a warm 0.44% aqueous solution of aminoazobenzene, and briefly rinsed, development with aniline or *b*-naphthol produces Soudan III on the fiber.

6. By impregnation for about 20 minutes with a hot, nearly saturated solution of *b*-naphthylamin in water, diazotization and development with *b*-naphthol produces azo Turkey red.

7. In a similar manner *a*-naphthylamin Bordeaux may be formed by diazotization and coupling with *b*-naphthol, after impregnation with *a*-naphthylamin, and reddish brown or reddish violet dyestuffs result with diazotized benzidin afterwards developed with *b*-naphthol.

8. Impregnation of either benzidin or dianisidin may also be accomplished with suitably concentrated solution of salts of the bases with the addition of the equivalent quantity of soda solution.

9. Bismark brown results when *m*-phenylenediamine is diazotized and developed, and other similar dyestuffs where the *m*-phenylenediamine is substituted by 1-3-5-toluylenediamine (so-called *m*-toluylenediamine).

10. Azochromin results when acetylcellulose filaments are treated with 0.5% aqueous solution of *p*-aminophenol at water bath

of stable dyestuffs, not fugitive to light, and resistant to dampness and perspiration. It is claimed this swelling of the fiber with inorganic acids materially increases the elasticity without accompanying hydrolytic dissociation, but the fact that insolubility in chloroform decreases and solubility in acetone increases by this treatment controverts the patentees contention.

Acetin has been claimed as an efficient assistant in the dyeing of cellulose acetate,[1] the solubility of the latter in the former causing the acetate to swell and become more porous, in which condition it readily fixes dyestuffs. Phenol, alcohol, acetone, glacial acetic acid and dichlorhydrin are preferably used as adjuncts to the acetin. Glyceryl triacetate may be replaced by other water-soluble esters of glycerol or the glycols.

H. Mork[2] has obtained patents for what is virtually a method of partial hydration of cellulose acetate, in which, by the action of dilute alkalis or alkaline carbonates, maximum acetylated cellulose is reduced in acetic acid content with a consequent change in solubility, especially in alcohol, acetone, acetylene tetrachloride, chloroform and glacial acetic acid. He claims that if fibrous cellulose triacetate in which the original structure of the cellulose has been substantially conserved, be allowed to stand with aqueous ammonia of specific gravity 0.90 for 15-16 hours at 10-20°, saponification gradually ensues, but can be stopped at points which approximate in acetic acid content to cellulose diacetate or monoacetate. When the diacetate stage is reached, the product is insoluble in alcohol, acetone, acetylene tetrachloride, glacial acetic acid,

temperature for about 10 minutes, then diazotizing and coupling with faintly alkaline pyrogallol solution.

11. In a similar manner naphthionic acid or preferably its alkaline salts as sodium naphthionate in about 3% aqueous strength is allowed to act upon the fiber for about 3 hours on the water bath. The absorption of the aminosulfonic acid is facilitated by the addition of acetic acid and sodium acetate. Real red E. is the final product.

1. Fürst Guido Donnersmarck'sche Kunstseide und Acetatwerke, D.R.P. 228867, 1907; abst. J.S.C.I. 1911, **30**, 21; Chem. Zts., 1910, **9**, 2138; Zts. ang. Chem., 1910, **23**, 2398; Chem. Ztg. Rep., 1910, **34**, 638.

2. E.P. 20672, 1910; F.P. 416752, 1910; abst. J.S.C.I. 1910, **29**, 1371; 1911, **30**, 354.

or chloroform. If, however, fibrous cellulose acetate be boiled with 0.4% aqueous sodium hydroxide for 2 hours, the acetate is then hydrolyzed to a solubility in the five reagents above named, and is considered to have reached the monoacetate stage. The three products are soluble in phenol. Among the suggested technical uses in addition to varying the solubility of the ester, is the application of this partial hydrolysis to films and sheets. Cellulose is acidylated to maximum acetylation, formed into films or filaments, the latter being then submitted to the limited action of a hydrolyzing agent. In this manner the filaments may be superficially converted into patterns or designs of the lower acetates, which possess hygroscopic and dyeing properties different from the triacetate. This partial conversion is stated to be especially advantageous in the case of backing films for photographic emulsions or for artificial silk which is subsequently required to be dyed.

It is not necessary to acetate cellulose before dyeing, for, it has been shown[1] that cellulose, cotton, starch, oxycellulose, hydrocellulose, etc., may be dyed full shades, the colors of which are not materially affected by the ingredients comprising the acetylating mixture. The coloring matters which are stable against the acid agents of the acetylating process are the dyestuffs of the algol, helindon, cibal, indanthrene, rosanthrene and certain sulfur colors, particularly those of the katigen and immedial groups. Rosanthrene A,[2] katigen brilliant green,[3] helindon scarlet S,[4] algol red B,[5] and

1. U.S.P. 994738, 1911; abst. J.S.C.I. 1911, **30**, 888. U.S. patent issued to E. Friedmann. E.P. 1556, 1911; abst. J.S.C.I. 1911, **30**, 1236, 1309. F.P. 427445, 1911; abst. J.S.C.I. 1911, **30**, 1051. D.R.P. 237210, 1910; abst. Zts. ang. Chem. 1911, **24**, 1837; Wagn. Jahr. 1911, II, 468; Chem. Zentr. 1911, **82**, 497. Belg. 233876, 1911. Aust. P. Appl. A-2376-11, Mar. 16, 1911; abst. Chem. Ztg., 1912, **36**, 252.

2. 200 parts of cotton dyed with 4% of rosanthrene A and developed on the fiber with the usual developers such as *b*-naphthol, *m*-phenylenediamine, are acetylated (preferably according to E.P. 21628, 1901) with 800 parts each acetic anhydride and glacial acetic acid and 20 parts sulfuric acid. The dark red solution is then precipitated with water, the cellulose acetate washed, dried and dissolved in chloroform. The solution leaves upon evaporation of the solvent, a clear, light red film.

3. 200 parts of cotton dyed with 10% katigen brilliant green is acetylized as above described, the chloroformic solution being of

indanthrene RS,[1] are specified as yielding especially dependable results. The acidylizing process is carried out in the regular manner, and when the acetylated cellulose is precipitated out in a large volume of water the dyestuff is also precipitated and gives full shades. Films dyed with these dyestuffs possess excellent fastness to light.

The dyestuff may be dissolved directly in the acetylating bath or in acetic acid and then added, according to the patented process of B. Borzykowski,[2] who dissolves direct dyestuffs as bismark brown, chrysophenine G., fast scarlet colors or substantive blacks and adds the solutions directly to the acetic acid-acetic anhydrid-vitriol acetating bath. Upon the introduction of the cellulose (cotton), the mixture is heated on the water bath until the acetylated cellulose passes into solution in the acetylizing mixture, after which it is precipitated out by water, benzol or alcohol, when a bright and clearly dyed acetated cellulose is said to result, which does not bleed into the precipitating bath, and possesses the same strength as in the uncolored condition. On treatment of the dyed cellulose acetate with chloroform, acetone, dichlorethylene, etc., a clear solution results which may be further treated without alteration of the shade.

L. Lederer[3] produces differential dyeing effects by com-

a green color and producing similarly colored films upon evaporation.

4. A brilliant vermillion red product results when 200 parts of cotton are dyed with 10% helidon scarlet S and then acetylized.

5. According to D.R.P. 184201, example 3, 100 parts of cotton dyed with 20% algol red B are acetylized with 400 parts of acetic acid anhydride and 1,500 parts of benzene. A red product is obtained which is soluble in chloroform.

1. 200 parts of cotton dyed with indanthrene RS are formylized with 100 parts of formic acid (an insufficient amount) and 3-10 parts sulfuric acid of 66° Be. strength according to D.R.P. 189836. From the deep blue solution obtained, the dark blue formylated cellulose can be precipitated and washed to neutrality in the usual manner.

2. E.P. 12995, 1912; abst. C.A. 1913, **7**, 3840; U.S.P. 1041587, 1912; abst. Mon. Sci. 1913, **79**, 110. Belg. P. 246562, 1912. D.R. Anm. B-63482, 1911. F.P. 444588; abst. Kunst. 1913, **3**, 15. See also E.P. 22826, 1913.

3. E.P. 11625, 1909; abst. J.S.C.I. 1909, **28**, 1030. F.P. 402072, 1909; abst. J.S.C.I. 1909, **28**, 1221. D.R.P. 240751, 1908; abst. Chem. Abst., 1912, **6**, 2179; Kunst., 1912, **2**, 215; Chem. Zentr. 1911, **82**, 1843. D.R.P. 248559, 1909; abst. Kunst., 1912, **2**, 296.

bining cellulose nitrates and acetates either before or after filament formation by means of mutual solvents as acetylene tetrachloride and acetone, or by weaving the filaments of the two esters. The difference in dyestuff absorption between the nitrates and the acetates may be increased by a denitration of the former, after which the entire material is immersed in a suitable dyebath containing coloring matters which will heighten the effect.

A. Wagner dyes fabrics of mixed colors in the piece, by covering a portion of the fibers with cellulose acetate before spinning,[1] or[2] spinning cellulose acetate fibers with filaments which possess different affinities for stated classes of dyestuffs. In this manner, after the pattern has been formed, the whole may be further waterproofed by spraying on an acetate or nitrocellulose lacquer.

A process evolved by Cross and Bevan[3] has for its object the treatment of cotton so that it may entirely resist the action of substantive dyestuffs, and is accomplished by superficially acetating spun cotton in such a manner that it is converted into lower acetyl derivatives without prejudice to the textile qualities of the fiber. The process consists in digesting the previously dried cotton with a mixture of glacial acetic acid, acetic anhydride and zinc chloride as the catalytic agent, the composition of the acetylating mixture varying with the degree of superficial acetylation required, the amount

See also Donnersmarck, D.R.P. Anm. 8m., D. 24553, Jan. 18, 1911, Method of Dyeing Formed Cellulose Acetate. See "Dyeing Artificial Silk of Cellulose Acetate," Text. Col. 1909, **31**, 264; 1910, **32**, 15.

1. D.R.P. 152217, 1901. Compare A. Sansone, "Dyeing Acetate Silk," D. R. Anm. S-31390, 1910.

2. D.R.P. 152432, 1901; abst. Zts. ang. Chem., 1904, **17**, 1252; Wagn. Jahr. 1904, II, 417.

3. Prize method in Jour. Soc. Dyers and Co., 1908, **24**, 189; abst. J.S.C.I. 1908, **27**, 802; Zts. ang. Chem. 1908, **21**, 2189; C.A. 1908, **2**, 2996. Process protected by following patents issued to C. Cross and J. Briggs: U.S.P. 920828, 1909; abst. J.S.C.I. 1909, **28**, 623. E.P. 5016, 1907; abst. J.S.C.I. 1908, **27**, 330; Mon. Sci., 1911, **74**, (5), 92; Farb. Ztg., **19**, 142; Bull. Soc. Chim., 1909, (4), **6**, 557. F.P. 383064, 1907; abst. J.S.C.I. 1908, **27**, 330. D.R.P. 224330, 1907; abst. Chem. Zts., 1910, **9**, 2105; Zts. ang. Chem. 1910, **23**, 2056; Chem. Zentr. 1910, **81**, II, 515; Chem. Tech. Rep. 1910, **34**, 448; Wag. Jahr. 1910, **56**, II, 434; Jahr. Chem. 1910, I, 426.

of zinc chloride used being from 10-20% of the mixture. The ratio of acetic anhydride to cotton will depend upon the degree of completion desired. The process is applicable to cotton fiber, either in the form of yarn or woven fabric, and is continued until acetate esters result, which, while still retaining the textile quality of the fiber or fabric, resist substantive cotton dyestuffs and can be subjected to alkaline lye in mercerization without being sensibly altered.[1] The different degrees of acetylation are controllable by keeping the ratio of acetylizing bath to cotton constant, and varying the concentration of the acetic anhydride.

1. In preparing the mixtures the liquid constituents are first mixed together and the zinc oxide is added in small quantities at a time, the mixture being stirred and cooled if necessary until all is dissolved. It is preferable, however, to employ zinc chloride directly rather than to attempt to produce it in the acetylating bath, and when the zinc chloride is used as such, a suitable mixture is prepared by dissolved 20 parts of commercial fused zinc chloride in 80 parts of glacial acetic acid with heat, the mixture forming a heavy, syrupy, clear liquid. 100 parts of acetic anhydride are next added, these proportions being suitable for a net gain in weight amounting to 20-40%, depending on the quantity of acetylating mixture used.

It will be understood that the degree of modification produced is not dependent solely upon the degree of dilution of the reagent. Thus smaller proportions of the more concentrated mixture will produce results equivalent to those obtained with a larger volume of the more diluted mixture. The ratio of acetic anhydride to cellulose is the important factor in calculating the yield. It is therefore evident that the proportions of acetic anhydride, acetic acid and catalytic agent may be modified within comparatively wide limits according to the nature of the material treated and the degree of modification to be produced.

When the cellulose material has been saturated with the reagent, the action may be accelerated by packing the material in a closed vessel which is then placed in a thermostat regulated at a temperature of 35-40°. After a period of 36 to 48 hours at this temperature, or a longer period if the material has been left at the ordinary temperature, the reaction is considered as complete. The acetated cellulose is then removed, washed with water until neutral, and until all soluble products have been removed. When it is desired to prevent shrinkage during the superficial acetylation, the hanks may be placed under tension as in mercerization.

When the cellulose is to be converted into a hard, nearly waterproof material corresponding with a gain of approximately 40-50% in weight, it should be treated with 3-4 times its weight of the more concentrated mixture or with a smaller proportion of a mixture higher in anhydride and containing less acetic acid. In the former case the cellulose should be turned over from time to time during the progress of the reaction in order that the excess of liquid may be uniformly distributed.

Suitable mixtures for a hard yarn may be made as follows:

		Mixture A. For net gain in weight of 25% on the cellulose.	Mixture B. For net gain in weight of 33%.
Acetic anhydride	(parts by weight.)	42.	56.
Acetyl chloride	"	11.5	11.5
Glacial acetic acid	"	50.	32.
Ignited zinc oxide	"	6.5	6.5
		110.	85.

For a gain in weight of approximately 25%, the dry cellulose may be caused to absorb twice its weight of mixture A, while for a gain in weight of approximately 33%, 1 part of cellulose may be caused to absorb 2.3 parts of mixture B. By varying the acetic anhydride concentration the fiber can be caused to gain in weight from 26-34%. In addition to resistance to substantive dyestuffs, the acetated fiber shows an increased affinity for basic dyestuffs, and will resist cold mercerizing to a sufficient extent to admit of differential mercerization of mixed fabrics. When applied to cotton in the piece the acetylation imparts a distinctive finish and firmness resistant to careful washing. In this manner industrial advantages accrue from the fact that the normal hygroscopic moisture of these acetylated cottons is only about one-half that of untreated cotton.[1]

Carbon Filaments from Cellulose Acetate. In a patent granted to A. Little[2] is described methods of utilizing the cellulose acetates in the preparation of filaments for incandescent lamps, whereby the percentage of carbon contained in the filaments is increased. In distinction from those filaments prepared from various fibrous materials such as bamboo, cardboard, cotton and linen thread and from certain forms of amorphous cellulose, in which it is difficult to prepare filaments of absolute homogeneity, and in which the carbon is

1. If a piece of partially acetated fabric treated by this process be immersed for three or four minutes in caustic soda solution of 40° Tw. strength, it is stated that the stripes of ordinary cotton are mercerized and shrink, while the stripes of acetylated cotton resist the mercerizing action. In this connection see Marsden, Jour. Soc. Dyers and Col., 1905, 21, 102, and editorial remarks thereon, Jour. Soc. Dyers and Col., 1905, 21, 192.

2. U.S.P. 532468, 1895.

distributed uniformly throughout their lengths, it is claimed filaments obtained by incineration of the cellulose acetates are substantially free from these defects, being especially free from inequalities in structure, unequal distribution of carbon, and variation in resistance of the filaments at different points.

Cellulose is first acetated, then dissolved, and either forced out of a small orifice into a coagulating medium, or the filaments are produced by evaporation of the solution on glass, drying the films so formed and finally cutting into strips. The strips or filaments obtained by either method are then carbonized and flashed in the usual manner. The patentee claims filaments made in this way show no inequalities in resistance.

Acetylated Cellulose in the Explosive Industry. A. Luck has obtained patent protection [1] for the use of the noninflammable cellulose esters in the smokeless powder industry as a modifier of the brisance of nitrocellulose and nitroglycerol explosives. According to his described process those nitroglycerol-nitrocellulose explosives like cordite, ballistite, the gelignites and blasting gelatin produce great heat on explosion, which in the case of firearms is a serious disadvantage, as the excessive heat injures the rifleing of the barrel. Luck has proposed to partially overcome the tendency to excessive heat of combustion and the tendency to instability by the introduction of substantial amounts of cellulose acetate, benzoate or propionate into the smokeless powder or explosive. When the acetate is mixed with the nitrate, the speed of combustion of the latter is said to be restrained. To a 13% nitrogen guncotton is added 25% by weight of cellulose acetate, which for a sporting powder may be shaped into grains and hardened in the usual manner. Nitroglycerol, dinitrobenzene and other bodies may also be incorporated, nitroglycerol being a direct cellulose acetate solvent.

E. Bouchard-Praceiq [2] indicates decomposition in smokeless powder by means of cellulose acetate or viscose. The powder grain is enclosed with an acetylcellulose film, which is impervious to the vapors of the ethyl or amyl compounds

1. EP. 24662, 1898. U.S.P. 649852, 1900.
2. F.P. 445770, 1912; abst. C.A. 1913, 7, 1976.

used for stabilizing, and this film is colored with an indicator which is affected by nitrous gases.

Cellulose Acetate as Insulating Material. Among the earlier patents for the application of the cellulose acetates is the process of E. Thomson and J. Callan,[1] in which the heretofore used collodion is replaced by an acetate lacquer as an insulating covering for electric conductors. It was found that wire coated with cellulose acetate was proof against moisture and moderate heat, and possessed a minimum thickness with relation to the size of the conductor. In insulating conductors by means of a fibrous material as cotton or silk braiding, the covering although heat-resisting to a certain extent is not moisture proof, while the compound coverings usually employed not only greatly increase the thickness of the conductor but do not hold up well, even under moderate heat. Cellulose acetate is capable or resisting a comparatively high degree of heat, is flexible, tough and not easily flammable, these properties rendering it suitable for magnet coils, and other purposes where the temperature may raise as high as 100-150°. The wire to be coated is uniformly covered by a plurality of thin coats, the cellulose acetate being preferably dissolved in a volatile solvent so that evaporation will be rapid after the acetate has been deposited upon the wire, the object being to set the acetate before it has had a chance to run and hence interfere with the uniformity of the coat. The apparatus recommended is shown in Fig. 502.[2] Adhesion to the wire

1. U.S.P. 695127, 1902; Reissue 11997, 1902. E.P. 2264, 1902; abst. J.S.C.I. 1903, **22**, 303. English patent issued to British Thomson-Houston Co., Ltd. Wire insulated with cellulose acetate according to this process is known in the trade as "Celestron."

2. In the accompanying figure, 1 represents a wire-reel, from which the wire is led across a grooved wheel 2, dipping in the coating bath. A number of these wheels are placed side by side, dipping in troughs containing solutions of the several compounds. The wire passes tangentially across a groove at the top of the wheel, the bottom of the wheel dipping in the coating material contained in the tank 3, divided into the desired number of chambers by transverse partitions. A scraper 4 may be employed to remove the excess of material from the coating groove which picks up the compound from the bath. A scraper 5 may also be employed in the bath to remove any dirt carried around on the wheel. After leaving each coating wheel, the wire passes through a hot-air box 6, which may be heated from gas jets leading from the pipe 7. After applying the

is increased by a preliminary coating of Canada balsam, Venice turpentine or rubber. In coating, the bare wire is led from a reel, preferably through a very thin solution of Canada balsam, which serves the dual purpose of dissolving any grease from the wire and covering it with a thin adherent coat which closely binds to the wire the subsequent acetate coat-

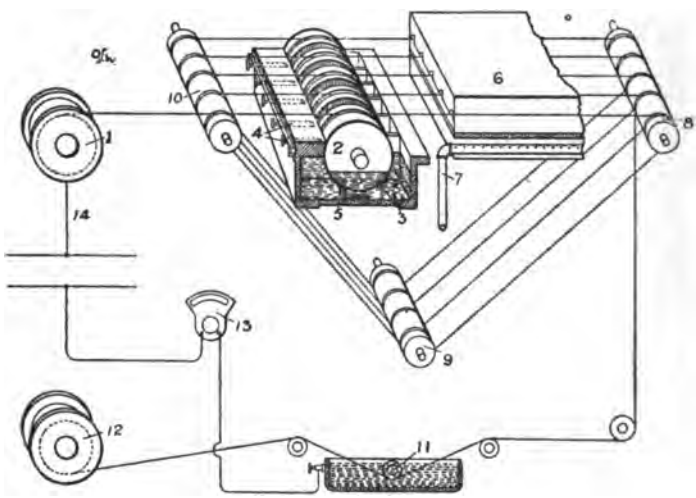


Fig 502. The Thomson and Callan Process for Insulation with Cellulose Acetate.

ings. The wire is led from the preliminary adhesive coating solution through a drying-box containing hot air, and into

first coat of balsam or other preliminary adhesive the wire is led through the drying box and over guide-sheaves 8, 9 and 10, back to the coating wheel, where the cellulose ester is applied, after which it again passes through the drying-box and over guide-sheaves to the third coating wheel, and so on in order until all the coats have been applied, after which it is led through a testing-bath 11, of mercury or other fluid conductor of sufficient depth around the wire and wound on a shipping-reel 12. The mercury bath is electrically connected with one terminal of a volt-meter 13, the other terminal of which connects with a circuit of the desired voltage The wire of the reel 1 is electrically connected by a conductor 14 with the other side of the testing source. Thus in case there is any defective spot in the insulation the voltmeter gives a visible indication, and the defect may be overcome before the wire is reeled. A suitable audible signal may replace or supplement the voltmeter.

another bath containing the primary cellulose ester coating compound. From this point the plurality of deposited coats is continued until the desired effect is produced. It has been found preferable to mix Venice turpentine in amount about equal to the actual amount of cellulose acetate in solution, this constituting the primary ester coat. Castor oil, phenol, or essential oils may be added where additional flexibility is desired.[1] This method has been carried on by the General Electric Company, at their Lynn, Mass., plant, and is described in detail in a recent communication by R. Fleming.[2] The insulation of fine wire in this manner is at

1. A softener composed of 5 parts by weight of castor oil, and 50 of phenol for each 100 parts of solid cellulose acetate is recommended.

2. According to R. Flemming of that company (General Electric Review, Jan., 1908; Eng. News, 1908, 59, 59) "insulated copper wire has become such a ruling factor in the design and manufacture of electrical apparatus that any process which reduces either the cost of the insulated wire, or the amount required, is of great commercial importance.

"Silk and cotton are about the only materials which have been used in the past for insulating purposes. The former is relatively expensive, while the latter, though cheap, unfortunately occupies a large proportion of the winding space, especially when the wire itself is small.

"Various chemical solutions have been applied to wires in the attempt to secure a thin, though permanent insulation, which would be more economical to use than silk or cotton.

"Cellulose acetate, enamel, collodion, casein, albumen, glue, rubber, silk, solutions, etc., were tried with more or less favorable results, but for commercial purposes cellulose acetate and enamel have proven to be the substances best adapted to the insulation of copper wires.

"The mechanical properties of the cellulose acetate film make it a desirable insulating medium for very fine wires. Its elasticity permits of considerable stretching of the wire before rupture takes place, thus insuring continuous insulation between wires on the finished coil. Its specific resistance is very high, so that the film, even though thin, provides ample insulation between turns and between the layers of superposed wire. The evenness of the coating, and the regularity with which the film can be applied to the wire, are important advantages; the finished wire is free from imperfection of coating, and presents an attractive appearance.

"This insulation can be colored any desired shade to harmonize with the surroundings. In case of very fine wire, a bright green makes a satisfactory color, rendering it easy for the operators to see the wire, and to detect irregularity in the winding; but if these fine wires are colored a neutral tint, they are practically invisible, and winding them is a difficult operation.

"The sizes of wire best suited to this process are from 0.003 in.

present one of the more important uses for cellulose acetate in the United States.

in diameter, or even finer, to those as large as .005 in. For larger sizes, the enamel coatings are more suitable.

"Cellulose acetate is especially valuable for the windings of meter armatures, where light weight is of great importance.

"The following tabulation shows some of the more important comparisons of data:

.033 Diam of Copper.	Acetate.	Single Silk.	Single Cotton.
Thickness of insulating film....	.0005	.0009	.00175
Wire space factor.....	.442	.313	.167
Wt. per thousand feet lbs.).....	.033	.036	.049

"With acetate coated wire the greatly improved space factor means, that for a given number of turns on a given form, the mean length of turn and total weight of wire are greatly reduced. This is shown in the following tabulation, which is drawn up on the basis of a perfect winding:

"Diameter of spool, 1 in.; Length of spool, 1 in.; Number of turns, 100,000; Diameter of copper, .003 in.

Insulation of Conductor	Outside Diam. of Coil (Inches).	Resistance (Ohms).	Weight of Coil (Lbs.).	Price per pound to give same cost of coil.
Acetate.....	4.20	71300	2.22	$7.50
Single silk.....	5.53	89500	3.04	5.50
Single cotton.....	9.50	144000	6.73	2.50

"Another advantage of acetate wire is that it is not affected by ordinary atmospheric conditions, whereas all fibrous materials absorb large quantities of moisture. Complete drying and impregnating processes are necessary for fibrous insulations, if long life is to be expected of them.

"Manufacturers of telephones and other specialties, who use fine wires, find film-coated wires of great service in reducing the cost, and also the size, of their apparatus.

"In the Lynn acetate wire-coating machines the solution automatically passes from the mixing reservoirs to the coating portion of the apparatus. Here, by a system of transfer wheels, the solution is applied to the revolving coating roll, which, in turn, deposits it on the moving wire. The quantity of solution placed on the wire must be adjusted to a nicety; therefore mechanical scrapers are employed, which remove the excess and leave just the proper amount to be deposited on the wire.

"After receiving its coating of solution, the wire passes through the oven at the rate of several hundred feet per minute. The volatile solvent is here driven off and the coating hardened, after which the process is repeated until numerous coatings have been applied. This method insures an even distribution of the film over the whole surface of the wire.

"To keep the fine wire moving at such a high rate of speed, a very delicate adjustment of the moving parts is required, for the

In a subsequent patent[1] a less expensive coating composition is claimed, which will at the same time add inappreciably to the bulk of the conductor, will have high insulation and will not deteriorate at ordinary temperatures. Collodion (nitrocellulose in solution), although less expensive than acetated cellulose solutions, possesses the well known defect of attacking the metallic wire upon the development of a slight acidity. To obviate this, and still take advantage of the cheaper nitrocellulose, the wire is first coated with acetylcellulose, then with a plurality of collodion coats as shown in Fig. 503, as many primary layers of the cellulose ester[2] being applied as is deemed necessary to effect a complete exclusion of the subsequent layers of collodion from the metal. After this preliminary treatment there are superposed as many layers of collodion, either plain or mixed with other ingredients as camphor.

The General Electric Co.[2] manufacture bushings especially adapted for insulating the shafts of Thomson recording watt-meters. The ends of the wire of required diameter for the ends of the bushing are joined together and then run continuously through baths containing the cellulose acetate liquid insulating material until the thickness of the series of coatings thus applied to the wire is sufficient to insure proper insulation. Precaution should be exercised to prevent the coating from adhering too tenaciously to the wire, in order that its subsequent ready removal from the wire may be assured. The coating is removed from the wire by stretching the latter to reduce its diameter, using for this purpose a wire made of lead or other non-resilient alloy.

The electrical insulating properties of the cellulose acetates are far superior to either rubber or gutta percha. Copper wire of 0.07-0.17 mm. diameter is the range usually insulated, the number of coats, the concentration of the acetate lacquer, and the speed of drawing the wire through the solution being so adjusted that a coat is applied of about 0.02 mm. in thickness, i. e., the wire is increased in diameter by about 0.04 mm.

slightest unevenness of motion is sure to break the wire. This is prevented by friction drives and friction tension devices, which insure a perfectly uniform motion.

1. U.S.P. 792001, 1905.
2. E. 19565, 1902. Cf. E.P. 11997, 1902.

Wire thus coated not only possesses a high insulating capacity, but is more compact and has an extremely low specific induction. The lacquer adheres to copper with great tenacity, especially in the presence of an intermediate coat of Venice turpentine or Canada balsam. Unlike the cellulose nitrate coatings, there is practically no danger of the copper being attacked and turning green. Any slight tendency of the acetate to eliminate acetic acid upon long standing may be obviated by the addition of a small amount of ant-acid to the lacquer, such as urea or pyridine. Cellulose acetate is especially valuable in the coating of telephone wires where a minimum specific inductive capacity is required.

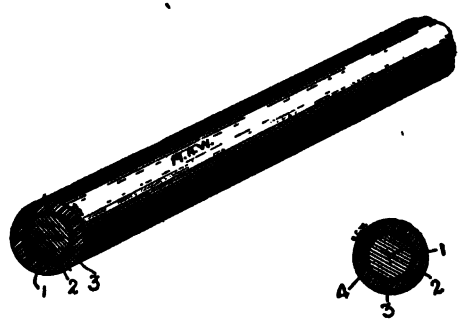


FIG. 503. FILM COATED WIRE (CALLAN PROCESS)

Dyestuffs may be added to the coating lacquer, wire so coated being found in the trade of a green color, due to the use of such basic colors as Victoria green, methyl green, which are readily soluble in the solvents of acetylated cellulose. The cellulose acetate may also be dyed before acetylation, as explained under Dyeing.

The Societe Debauge et Cie [1] have described a cellulose

1. F.P. 418347, 1909; abst. J.S.C.I. 1910, **29**, 1117; 1911, **30**, 96. In addition No. 15217 to F.P. 418347 (abst. J.S.C.I. 1912, **31**, 651; Kunst., 1912, **2**, 316) is described the preparation of an infusible insulating varnish for electric construction and wire

acetate lacquer especially valuable for electric construction, and composed of a tetrachlorethane solution of cellulose acetate to which a small amount of pyridine has been added. In their prescribed formula 6-12 parts of acetylcellulose are dissolved in 93-87 parts of tetrachlorethane, 0.5-1 part of pyridine being subsequently added. The object of the pyridine is stated to neutralize any trace of acetic acid that might subsequently be liberated, and if given off would tend to attack the copper or other insulated metal and cause ultimately a defective insulation. The viscosity of the solution may be augmented by the addition of solutions of aldehydes of the terpene series such as camphor, fenone or carvone, or by the solid body hexachlorethane. It is claimed that the combination of pyridine with cellulose acetate, either with or without hexachlorethane, produces a lacquer when incorporated with tetrachlorethane which will withstand a temperature of 200° without causing deterioration of the cellulose ester lacquer. The lacquer is stated as especially suitable for the insulation of electric conductors and in uniting a number of finer wires as in cable manufacture.

H. Zwick [1] has described the preparation of a cellulose acetate dip lacquer especially useful for insulation purposes.

The Societe D'Exploitation des Brevets Dolter [2] insulate metallic and other pieces by first cleaning, scouring and drying the metal, and then spraying over or brushing on cellulose acetate dissolved in chloroform, acetone, nitrobenzene or ethyl or amyl acetates, the latter being a non-solvent. The thickness of the coating is regulated by the concentration of the lacquer, or by the number of coatings applied. Better results

covering, in which cellulose acetate and hexachlorethane are mixed in about equal parts, the absorption of the latter by the former being produced by means of a common solvent such as tetrachlorethane. Other solvents such as alcohol or acetone may be used in addition.

1. D.R.P. 211520, 1907, Zwick, abst. Zts. ang. Chem. 1909, **22**, 1558; Chem. Zentr. 1909, **80**, II, 398; Wagn. Jahr. 1909, II, 541, covers the use of cellulose nitrate for the above described purposes, whereas DR.P. 211573, 1907, being addition to D.R.P. 211520; abst. Zts. ang. Chem. 1909, **22**, 1558; Chem. Zentr. 1909, **80**, II, 399, describes the use of cellulose acetates for the same purpose.

2. F.P. 375092, 1907; abst. J.S.C.I. 1907, **26**, 877.

are obtained by a number of thin coatings than by a fewer number of coats of higher concentration in cellulose ester. Each layer, of course, is carefully dried before the subsequent one is applied.

In order to preserve the wood used for posts in wireless signaling, M. Zelensky [1] proposes to first steep the boards in a cellulose acetate solution, after which the posts are spirally wound with canvas coated with viscose. The inside of the hollow post is finally waterproofed either with a mixture of resin, tallow and sulfur, or with pitch.

Realizing the fact that cellulose acetate is in common use as an insulating material for covering thin wires, A. Campbell [2] has made some tests with it with the view of comparing its properties in this respect with natural cellulose. The cellulose acetate used for the comparisons was soluble in chloroform, and was found to contain a small amount of sulfur in combination, probably as the SO_4H residue. Sample 1 when air dry gave a specific inductive capacity of 4.7, and upon drying the value was about 3.9. The variation due to temperature was scarcely perceptible, being about 1% for 40°. Sample 2 gave less consistent and somewhat higher values. The resistivity was also approximately determined with result of 200 volts with one minute electrification, the results being given in the appended table:

W. Viewig has given some figures as to the cost of covering wire with a cellulose acetate solution,[3] which have been called in question by W. Doht.[4] For proper insulation it is

Material.	Condition.	Temperature.	Resistivity. mega-megohm cm.
Cellulose acetate (1).....	Air-dry	16.5°	200
Cellulose acetate (1).....	Oven-dry	26.0	over 9000
Cellulose acetate (2).....	Air-dry	26.0	13
Cellulose acetate (2).....	Oven-dry	26.5	121

1. E.P. 2156, 1906.
2. Proc. Roy. Soc. 1906, 78-A, 196-211; abst. J.S.C.I., 1906, 25, 935; Chem. Centr. 1906, 77, II, 1184-1185.
3. Chem. Ztg. 1907, 31, 85; abst. Chem. Centr. 1907, I. 677.
4. Chem. Ztg. 1907, 31, 302; abst. Zts. ang. Chem. 1907, 20, 743.

given that wire of 0.1 mm. diameter requires 40-60 gms. of cellulose acetate for the proper insulating of 18000 meters. With wire of 0.07 mm. diameter, the same amount of cellulose acetate will insulate 25000 meters. To wind 0.1 mm. wire with silk requires about 120 gms. of silk.

The Compagnie Gen. D'Electricite[1] utilize cellulose acetate, formate, benzoate and sulfoacetate in the preparation of stereotypes by coating a sheet of paper with a thin layer of the cellulose ester saturated with a solvent of the latter. The softened sheet is then pressed upon the surface to be reproduced, and afterwards strengthened by the application of one or more layers of shellac.

P. Lagrange[2] waterproofs viscose products by coating the surfaces, on all sides, with a thin layer of nitro- or acetylcellulose.

McTavish, Ramsey & Co. and A. Ramsey have been granted patent protection for a process of producing artificial wood, which compared with existing processes must be unduly costly, and in which caustic soda, which is advocated in conjunction with acetylcellulose, must materially saponify the latter back to the original cellulose with the formation of sodium acetate. In their described method,[3] wood sawdust (so-called wood meal) is mixed with cellulose acetate and potassium or sodium hydroxide, wood lime or a mixture or soda and alum, treated with hot caustic alkali, dried and pressed.

The Societe Debauge[4] have described the uses of acetylated cellulose as an insulating material for cable impregnation. In the advocated process, bands, threads or films of cotton, paper or wood pulp or jute fibers are impregnated with cellulose acetate solution under pressure, to which plastic-inducing materials may be added.

Cellulose Acetate for Toughening Incandescent Mantles. In the manufacture of incandescent mantles of the Welsbach and similar types, it is necessary to stiffen the rare earth

1. D.R.P. 272695, 1911; abst. C. A. 1914, **8**, 2786.
2. F.P. 463613, 1912; abst. C.A. 1914, **8**, 2805.
3. E.P. 7038, 1913; abst. Kunst. 1914, **4**, 237.
4. F.P. 453564, 1913

oxides by means of a solid coating, to insure their safe transportation and handling without injury. After the original mantle fabric has been impregnated with solutions of rare earth salts, the fabric (usually cotton) is ignited, leaving a delicate reticulated skeleton of the corresponding oxides, which are exceedingly fragile. For many years it has been customary to immerse such mantles in a pyroxylin solution and allow the solution to dry to reinforce the mantle. J. Hirsch proposes [1] to use a solution of cellulose acetate as the toughening fluid, preferably that partially hydrated ester which is soluble in alcohol. The lacquer is prepared by dissolving 25 parts of acetylated cellulose, 3 parts each of camphor and castor oil in 100 parts of alcohol. The inflammability may, if desired, be increased by the addition of a small amount of nitrocellulose dissolved in acetone or other liquid miscible with the acetylcellulose solvent.

Acetic Colodion. Until quite recently this term has been restricted to solutions of nitrocellulose in concentrated acetic acid, and has found its principal use as a dip to impregnate and stiffen Welsbach and similar incandescent gas mantles. Acetic acid solutions are considered more penetrative than amyl acetate or acetone solutions, and in addition are very uniform in drying, which preserves the shape of the finished mantle without distortion. It has been customary to modify the inflammability of the lacquer due to the presence of the nitrocellulose by the addition of difficultly inflammable material which was at the same time soluble in glacial acetic acid, gelatin being most satisfactory. The principal drawback to the use of gelatin in this connection is its hygroscopic tendency and ready solubility in water. The replacement of gelatin by cellulose acetate overcomes this objection, both the cellulose nitrates and acetates being soluble in glacial acetic acid. Variation in the amount of acetic ester to cellulose nitrate governs the speed of burning, whereby the inflammability may be varied within wide limits, the preparation being entirely water insoluble, not hygroscopic and permanent in the atmosphere under all normal weather conditions. Paraffin

1. F.P. 324718, 1903; abst. J.S.C.I. 1903, **22**, 620.

would undoubtedly be suitable, but it is insoluble in acetic acid. Where the speed of ignition of the mantle is too great, it has been found that often the interstices between the woven filaments expand to such an extent as to rupture the knitted fabric, or the rare earth salts which were deposited upon the ignition of the fabric.

A. Plaissetty [1] spins an acetic acid solution of a cellulose ester directly into filaments, the acid being capable of holding the incandescent salts in solution. The advantages claimed for acetic acid over a mixed lacquer solvent is the uniformity in drying due to the presence of a single evaporating body.

Cellulose Acetate Photographic Emulsions. Considering the volume of experimentation which has been done in adapting nitrocellulose solutions to photographic purposes, it seems a quite natural sequence of thought that the cellulose acetates might replace collodion in the preparation of photographic emulsions. Edward Valenta was the first to record experiments in this direction,[2] the cellulose acetate which he used being insoluble in alcohol and acetone, from which it appears that he used an acetate which had been but little hydrated.[3]

1. E.P. 26381, 1897; 3770, 1898; 63, 1899; 9088, 1900; 20747, 1901; F. P. 321803, 1902; U.S.P. 768073, 1904; abst. J.S.C.I. 1899, **18**, 479, 746; 1901, **20**, 699; 1902, **21**, 1389; 1903, **22**, 547; 1904, **23**, 897.

2. Photo. Corr. 1901, 305; abst. Eder's Jahr., 1902, 582-583; Chem. Centr. 1901, **72**, II, 40; Jahr. Chem., 1901, 891.

3. The cellulose acetate with which he worked was a flocculent mass of greyish-white color with faint odor of nitrobenzene, soluble in chloroform, a 5-10% of which was quite dark in color and cleared slowly. It is evident therefore that Valenta worked with an impure product. He further states that it was soluble in epichlorhydrin, nitrobenzene and glacial acetic acid. From the latter solution it is precipitated by water or alcohol in translucent gelatinous flocks, insoluble in acetone, ether, alcohol or benzene. A chloroform solution may be diluted with acetone without precipitation and with smaller amounts of alcohol without becoming turbid. Pure solutions in chloroform proved unsuitable for the manufacture of emulsions because the chemicals required to be added while soluble in alcohol were insoluble in chloroform. More concordant results were obtained with chloroform solutions diluted with large volumes of acetone. With certain precautions the acetone-chloroform solutions gave emulsions which coat well and give useful printing papers. The printing papers obtained showed a smooth even film, and a sensitiveness lying between that of albumen paper and a good collodiochloride paper. The film allowed the ordinary toning and fixing solu-

The next year the Farbenfabriken vorm. F. Bayer and Co.[1] patented the following formula for a print-out emulsion:

A solution of 3 parts of magnesium chloride and 1.5 parts of nickel chloride dissolved in 40 parts of water is mixed with 60 parts of alcohol. This mixture is added to 1000 parts of a 2% alcoholic solution of the acetylized cellulose soluble in alcohol.[2] After stirring for some time, the two following solutions are added—with stirring: First, a solution of 20 parts of silver nitrate in 40 parts of water is mixed with 60 parts of alcohol, and then a solution of 5 parts of citric acid in 40 parts of water is mixed with 60 parts of alcohol. When the mixture has become homogeneous it is filtered if necessary, and is then in condition to be employed for coating glass plates, papers and similar materials. It is claimed that paper coated with acetate emulsion in this manner has the advantage over celloidin and other nitrocellulose papers in that they possess a greater brilliancy, a finer grain, and better resistance to external influences. They are distinguished from the albumen papers by greater stability.

In the preparation of sensitized plates, films and printing paper by the I. Hoffsummer process,[3] the paper is treated with cellulose acetate prior to being coated with the emulsion, the object being to so sufficiently waterproof the paper that it will not absorb the emulsion, and yet cause the latter to strongly adhere to it. The patentee has described a similar

tions to penetrate easily and the film appeared to adhere firmly to the support. The films may be readily retouched in the usual manner.

1. E.P. 25821, 1902; F.P. 326463, 1902; abst. J.S.C.I. 1903, **22**, 820; D.R.P. 169364, abst. Chem. Centr. 1906, **77**, II, 187. Wagn. Jahr. 1906, II, 485. U.S.P. 752388, 1904.

2. As prepared according to D.R.P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr., 1904, **75**, II, 625; Jahr. Chem., 1904, 1168; J.C.S., 1904, **86**, 853. D.R.P. 159524, 1901; abst. Chem. Centr., 1905, **76**, II, 527; Zts. ang. Chem., 1905, **18**, 1636; Jahr. Chem., 1905-1908, II, 984; J.C.S. 1906, **90**, 6. E.P. 21268, 1901; abst. J.S.C.I., 1902, **21**, 870. F.P. 317007, 1901; abst. J.S.C.I. 1902, **21**, 870; Mon. Sci., 1903, (4), **60**, 54. U.S.P. 734123, 1903; abst. J.S.C.I. 1903, **22**, 961; Mon. Sci. 1903, (4), **60**, 173. U.S.P. 790565, 1905; abst. J.S.C.I. 1905, **24**, 686. It. P. 31391. Can. P. 62042, 1901.

3. E.P. 3855, 1904; abst. J.S.C.I. 1904, **23**, 622. F.P. 357473, 1905; abst. Mon. Sci. 1907, **67**, 43.

method in which nitrocellulose is substituted for acetated cellulose.[1]

In the foregoing described process those cellulose acetates soluble in alcohol are recommended. L. Lederer has found out [2] that other cellulose acetates are equally applicable, especially those soluble in glacial acetic acid, which is substantially all the cellulose acetates at present known. He goes a step further and claims to be able to use directly the mass obtained by the acetylation of cellulose, provided the condensing medium has been properly neutralized. The possible inhibition due to the salts introduced to neutralize the condensing medium is not explained away.

In preparing the acetic acid emulsion according to Lederer, 1000 cc. of a 2.5% solution of cellulose acetate in acetic acid is added to 35 gms. of a mixture of crystallized strontium chloride (45 parts), anhydrous lithium chloride (1.5 parts), water (9 parts), and absolute alcohol (20 parts). To the mixture thus produced is next added 25 gms. glycerol which has been mixed with 25 gms. absolute alcohol, after which a jet consisting of 30 gms. of silver nitrate dissolved in a mixture of 40 gms. of water and 75 gms. of absolute alcohol is caused to run into the acid mixture with continuous shaking. After all materials have been intimately mixed by shaking, a solution of 10 gms. of citric acid in 40 gms. of absolute alcohol is finally added. The cellulose acetate chlorocitrate emulsion thus obtained may be poured on a proper base or support in the usual manner, the impregnated sheets being then suitable for photographic purposes. Lederer points out that this may be applied either to a cellulose nitrate or acetate film, to either of which it will adhere and unite, due to the action of acetic acid, a mutual solvent of both the nitric and acetic esters.

Composite films for use in the "bleach out" process of color photography [3] are made to consist of a layer of cellulose

1. See E.P. 25390, 1903; abst. J.S.C.I. 1904, **23**, 337.

2. E.P. 26503, 1906; abst. J.S.C.I. 1907, **26**, 1295. F.P. 371358, 1906; abst. J.S.C.I. 1907, **26**, 344; Mon. Sci., 1908, **69**, 150. D.R.P. 191326, 1906; abst. Wag. Jahr. 1907, II, 507. Belg. P. 195837, 1906.

3. J. Smith and W. Merckens, E.P. 2461, 1907; abst. J.S.C.I. 1907, **26**, 1109. Belg. P. 198836, 1907.

acetate containing the basic dyestuff and a layer of gelatin, glue, isinglass, casein or analogous material, which contains the acid dyestuffs. The films may also consist of a cellulose acetate layer containing three basic dyestuffs on a gelatin base, or three acid dyestuffs supported on cellulose acetate.[1] A final sensitizing with hydrogen peroxide is required, as the sensitizers first used remain in the cellulose ester layer.

In the preparation of dark-room light filters it is difficult to obtain glass which is satisfactory, while gelatin filters must be protected from extremes of dampness and heat and are very prone to split. The advantage of a cellulose acetate sheet as a dark-room light filter is that, as it is insoluble in water and non-hygroscopic, it is unaffected by atmospheric extremes, and has also sufficient flexibility and tenuity so that in ordinary usage there is practically no liability of tearing.

Acetylcellulose Sheets. The art of making cellulose acetate films in sheets was clearly described by C. Waite in 1901,[2] the acetated cellulose being combined with lactic acid used both as solvent and to impart flexibility and softness. E. Zuehl[3] formed sheets of the desired pliability by the use of naphthyl acetate in conjunction with acetylcellulose. L. Lederer advocates the use of resorcinol diacetate[4] for the same purpose, but the hygroscopicity and slight solubility in water of this body renders its successful use attended with difficulty. A patent was applied for but not granted[5] for the formation of acetate

1. As an example, a 3% collodion or cellulose acetate solution is added to an alcoholic solution of auramine, erythrosine, and methylene blue until a drop of the mixture placed on a gelatin coated surface dries to a neutral grey color. An alcoholic solution of anethol or other sensitizer or mixture of sensitizers is added, and the emulsion coated on gelatin covered paper. When dry the erythrosine has passed into the gelatin, the two basic dyestuffs remaining in the cellulose ester layer.

In general, any gelatin emulsion should contain a considerable percentage of alcohol or acetone, so the latter will penetrate into the underlying acetylcellulose support, upon which the gelatin is placed. For statement of acetate films by Eastman Kodak Co., see Jour. Ind. Eng. Chem. 1911, **3**, 530, 841, 871.

2. U.S.P. 690211, 1901.

3. U.S.P. 729990, 1903. D.R.P. 162239, 1902.

4. E.P. 8945, 1909; abst. J.S.C.I. 1909, **28**, 1271. F.P. 402083, 1909; abst. J.S.C.I. 1909, **28**, 1270.

5. H. Reeser, E.P. 12976, 1909; abst. J.S.C.I. 1910, **29**, 147. F.P. 411126, 1910, abst. J.S.C.I. 1910, **29**, 875.

sheets by precipitation by means of a mixture of alcohol and benzene, rolling out the acetylated ester by mechanical means into sheets of the desired dimensions. In carrying the process into effect, 2 parts by weight of acetylcellulose soluble in ethyl acetate are mixed with 20 parts of methylated spirit and 20 parts of benzene. The mixture is heated to 60° on the water bath for some time, then to boiling, the acetylcellulose after a time suddenly passing into solution, and on cooling forming a gelatinous mass which may be rolled into durable sheets after the addition of 6 parts of camphor and 4 parts of aceto-chlorhydrin.

H. Cathelineau and A. Fleury[1] combine acetylcellulose with casein and phenols, such as phenol, cresols or guaiacol. Three parts of phenol are mixed with one part of casein, and after the mixture is allowed to stand for 24 hours, it is heated on the water-bath. The limpid fluid thus obtained is incorporated with cellulose acetate in sufficient amounts to obtain the desired tenacity and elasticity. While still warm, the mixture is poured into sheets and allowed to harden by cooling. Lederer prepares films for photographic purposes by combining nitrocellulose solutions of acetylcellulose by means of the mutual solvent mixture of acetone and tetrachlorethane, afterwards, if desired, decreasing the inflammability of the finished film by denitrating the pyroxylin.[2] Where 3 parts of nitrocellulose to 1 part of the acetic ester is used, the inflammability is said to be so low that denitration may be safely dispensed with.

In a patent recently issued to H. Mork[3] is described a method of acetylcellulose sheet formation said to be especially advantageous for photographic films, in which the acetylated cellulose is partially hydrated while in the film state, by means

1. F.P. 354942, 1905; abst. J.S.C.I. 1905, **24**, 1169. Addition thereto dated June 8th, 1905; abst. J.S.C.I. 1905, **24**, 1226. E.P. 12277, 12278, 1905; abst. J.S.C.I. 1906, **25**, 327. D.R.P. 185240, 1906; abst. Chem. Zentr. 1907, 1037; Zts. ang. Chem. 1907, **20**, 2177. D.R.P. 185241, 1906; abst. Chem. Zentr. 1907, 1819.

2. E.P. 11625, 1909; abst. J.S.C.I. 1909, **28**, 1030. F.P. 402072, 1909; abst. J.S.C.I 1909, **28**, 1221.

3. U.S.P. 1061771, 1913; abst. Kunst. 1913, **8**, 436; Mon. Sci. 1914, **80**, 23.

of dilute alkalis or acids, the patent claiming the partial hydration of the seasoned surface admits of a better adhesion of the emulsion.

In a later process[1] Mork describes the preparation of filaments, films and sheets by precipitating a solution of acetylcellulose in acetylene tetrachloride, either alone or in conjunction with methyl or ethyl alcohol[2] by means of kerosene or other petroleum hydrocarbon, selecting that petroleum fraction the average boiling point of which is higher than that of acetylene tetrachloride. By proceeding in this manner, the patentee claims, threads so produced do not shrink so much on drying as when methyl or ethyl alcohol is used as the coagulant.

In the formation of acetate films from the evaporation of solutions, they are prone to become wrinkled and distorted during drying, due to air currents, unless great care is exercised. Too rapid evaporation of the solution or the use of large amounts of low boiling and hygroscopic solvents will produce the same effect. This may be greatly minimized by guarding against air currents as by laying a cloth over a frame covering the plate upon which the film is being dried, the object being to allow the evaporation to take place surrounded by solvent vapor. All solutions intended for film formation should, of course, be allowed to stand for some time to insure that all air bubbles have arisen to the surface.

In the preparation of acetate films and sheets, if they detach from the glass with difficulty, a little water introduced under the edge of the film will so loosen the acetylcellulose that it may be gradually removed, and if immediately after its removal the sheet be placed between bibulous paper under pressure, the film will dry with no appreciable distortion. Acetate films when stripped green and allowed to dry in the air, possess about 10% greater tensile strength then when allowed to dry on the casting surface.

A mixture of gelatin, alcohol and glacial acetic acid is

1. U.S.P. 1107222, 1914; abst. J.S.C.I. 1914, 33, 958; C.A. 1914, 8, 3371.

2. Cf. U.S.P. 1009116, 1911; U.S.P. 1035108, 1912.

the proper adhesive to attach gelatin films to acetylcellulose, the acetic acid being an energetic solvent of both. The acetic acid must not be so concentrated as to soften and buckle the acetate film. The value of the alcohol is in sufficiently softening the acetate to roughen the surface and hence admit of a thoroughly firm adhesion of gelatin and acetate.

H. Danzer [1] prepares cinematograph films and bands by superficially acetating cellulose to render it impermeable to water. After acetation the films are subjected to treatment with acetone or other appropriate solvent to dissolve the portion of the band which has been converted into acetate. In another process [2] gelatin, viscose or other films are made and these given a coating of cellulose acetate, the object being to insure the greatest degree of non-inflammability.

The A. Lumiere film [3] is prepared by applying to a polished surface a thin layer of cellulose acetate, then a layer of gelatin, and finally a photo emulsion. The cellulose acetate layer need not be more than one-fifth to one-half the thickness of the entire film. Especially when the gelatin is given a toughening treatment with chrome alum or formaldehyde, films prepared in this manner are said to be unaffected in dimensions by the subsequent development, washing and other treatments to which they are necessarily subjected.

P. Hewitt [4] prepares a fluorescing mass for transforming light rays consisting of a flourescent dyestuff, a binding agent, and a material containing the light-transforming properties of the mass. Cellulose acetate is employed as the binding agent. V. Henri [5] has studied the action of ultra violet rays upon various materials and has demonstrated that the action of ultra violet rays is not continuous. He records the results of experiments of the passage of ultra violet rays through such

1. E.P. 3603, 1910; abst. J.S.C.I. 1910, **29**, 978. F.P. 410725, 1909. First Add. dated Mar. 18, 1910, to F.P. 410725; abst. J.S.C.I. 1911, **30**, 925. E.P. 14407, 1909; abst. J.S.C.I. 1909, **28**, 1327. See also U.S.P. 988981, 1911. D. R. Anm. 25533, 1911.

2. Balland et Cie, F.P. 457925, 1913; abst. J.S.C.I. 1913, **32**, 1033.

3. F.P. 401228, 1908; abst. J.S.C.I. 1909, **28**, 1064.

4. D.R.P. 254083, 1911; abst. C.A. 1914, **8**, 1065.

5. Compt. rend. 1912, **155**, 315.

substances as cellulose acetate, quartz, glass and viscose films.

In distinction to the usual method of preparing films, consisting in dissolving the raw material in a suitable solvent, then spreading the solution on a flat base, allowing the liquid to evaporate, the residue being left behind in the shape of a film, Knoll and Co.[1] have found that films may be prepared from acetylcellulose solutions containing solvents miscible with water (such as acetic acid), if these solutions are spread on a suitable supporting base, and then the base with the solution thereon, dipped in a precipitating liquid such as water.

The films thus obtained, even when of considerable thickness, are said to be clearly transparent and highly elastic. This process offers the advantage that it is possible to use solutions of acetylcellulose directly from the acetylizing bath, for film manufacture. If precipitants other than water are used, they must be miscible with the cellulose acetate solvent. In practice, glacial acetic acid has been found the most satisfactory solvent.

Continuous Photographic Films. These differ but little from the sheet films just described except in mechanical arrangements for producing them in lengths of 500 to 1000 feet, and longer. Not only roll-film photography, but especially chrono-photography, popularly called Moving Pictures, has developed into such great prominence and become such an important and well recognized factor in the amusement of the world, that the more meritorious methods for the preparation of these films will be described briefly. With increasing numbers of moving picture amusement places came increased responsibility due to the inflammability of the nitrocellulose continuous films used therein, and hence the use of an uninflammable material, as cellulose acetate, has been the subject of most painstaking and exhaustive research in attempts to replace the more combustible nitrocellulose and celluloid films by those of acetated cellulose, which burn no more energetically than unaltered cellulose. The credit for the prepara-

1. E.P. 3559, 1910; abst. J.S.C.I. 1910, **29**, 1082. F.P. 412503, 1910; abst. J.S.C.I. 1910, **29**, 1038. Aust. P. 41831, 1907; Phot. Ind. 1912, 509; Eder Jahr. Phot. 1911, 498.

tion of a cellulose ester film in long lengths should be given to Rev. Hannibal Goodwin, of Newark, New Jersey, who filed in the United States patent office on May 2, 1887, an application for a "Photographic Pellicle and Process of Producing Same." This application, after being held up until September 13, 1898, eventually issued as U. S. Patent 610861.

The validity of portions of this patent, and the priority of conception as disclosed therein, has had recent important legal sustainment, but has, as yet, not been adjudicated. He claims a process in which cellulose ester pellicles may be made in lengths of indefinite extension and width, sufficiently long to receive thereon a multiplicity of impressions. This was accomplished practically by flowing a pyroxylin solution upon a long, polished and scrupulously clean glass surface, in an atmosphere substantially free from dust and convection currents, varying the solvent portions of the formulae to admit of minimum hygroscopicity by means of such high-boiling, non-hydrous, non-hygroscopic eventual solvents as nitrobenzene and amyl acetate, combined with water-repellent non-solvents as benzene and the petroleum hydrocarbons. The breadth of interpretation of some of the claims of this patent is still under legal review.

Two years after the filing of Goodwin's application, and nine years before its issuance, and hence nine years before Goodwin's process supposedly became public, H. Reichenbach received patent protection for a similar process [1] for the manufacture of flexible photographic films in continuous lengths, in which the ideas of Goodwin were substantially duplicated, with the exception of the advocated addition of large amounts of fusel oil, which, it may be stated, was never done in practice. In this method the cellulose ester in solution was spread or flowed upon a glass or other rigid supporting surface, with a traveling carriage carrying a hopper for the fluid solution.

J. Stevens and M. Lefferts [2] made important advancements in producing continuous photographic sheets. They apparently appreciated the fact that the great advantage in the

1. U.S.P. 417202, 1889; 599631, 1898; 619617, 1899. See also Reichenbach and S. Pasavant, U.S.P. 458663, 1891.

2. U.S.P. 573928, 1896.

use of glass plates for the formation of photographic films lies in the fact that the smoothness of the glass enabled a film equally smooth to be peeled from it, while the vitreous surface was unaffected by traces of acid. They later substituted for glass an equally smooth metallic surface in the form of an endless band or belt, upon which the solution was deposited, spread and dried while the belt was still in motion. The congealed or hardened film was then stripped from the belt before the latter had made a complete revolution, thus furnishing a means of producing continuous sheets of great regularity and rapidity, and of practically unlimited length. They also attempted the recovery of the evaporated solvents with a commercial degree of success.

In the F. Anthony film manufacturing process,[1] the cellulose ester having been dissolved, clarified and reduced to the desired state of limpidity, was fed by means of a slit in a hopper with micrometer gauge onto a revolving drum with steam heating arrangement, and was wound up in a congealed state before the drum had made an entire revolution. R. Anthony,[2] J. Thornton,[3] Thornton and Rothwell,[4] F. Cossitt,[5] B. Edwards, G. Hue,[6] M. Ratignier and H. Pervilhac Co.[7] and the Soc. Civile des Pellicules Nouvelle pour Cinematographes[8] made substantial improvements, mostly in mechanical refinements.

According to the coagulation process of the Soc. Gen. des Films and C. Gonon[9] for continuous film formation, a very

1. U.S.P. 726614, 1903.
2. U.S.P. 735436, 1903.
3. E.P. 5793, 1899; abst. J.S.C.I. 1900, **19**, 559.
4. J.S.C.I. 1900, **19**, 157, 274, 689; 1901, **20**, 68; 1904, **23**, 680.
5. U.S.P. 864123, 1907.
6. E.P. 19437, 1902.
7. F.P. 391785, 1908; abst. J.S.C.I. 1908, **27**, 73, 444. See also W. Walker E.P. 4214, 1893; Sandell Films and Plates Ltd., and W. Smalley E.P. 25243, 1902; and O. Mohr, D.R.P. 204868, 1906; U.S.P. 953175 for other methods of continuous pyroxylin film formation.
8. F.P. 384111, 1907; First, Second and Third Add. thereto dated Jan. 28, and Feb. 1, 1907; Fourth Add. thereto dated Aug. 31, 1907; F.P. 384112, 1907; First Add. thereto dated July 6, 1907; abst. J.S.C.I. 1908, **27**, 471, 1081, 1220.
9. F.P. 388755, 1908; abst. J.S.C.I. 1908, **27**, 959. See J. Chaubet E.P. 14525, 1899.

soluble ester is dissolved in methyl alcohol or other suitable solvent of quick evaporative tendency, and this is delivered through a slit onto a band traveling beneath the surface of a coagulating liquid. This liquid must be miscible with the cellulose ester solvent, but must be a non-solvent of the ester, petroleum benzine being suitable. After the film passes through the coagulating bath it is still sufficiently plastic to be flattened and smoothed out by pressure between rollers. It is finally dried under tension in a current of air.

A. Lumiere et ses Fils [1] prepare noninflammable photographic films by applying to a polished surface a thin layer of cellulose acetate, then a layer of gelatin, and finally a photo emulsion. The cellulose acetate layer need not be more than one-fifth to one-half the thickness of the entire film. Prepared in this manner, it is said the film is unaffected in dimensions by the subsequent treatment.

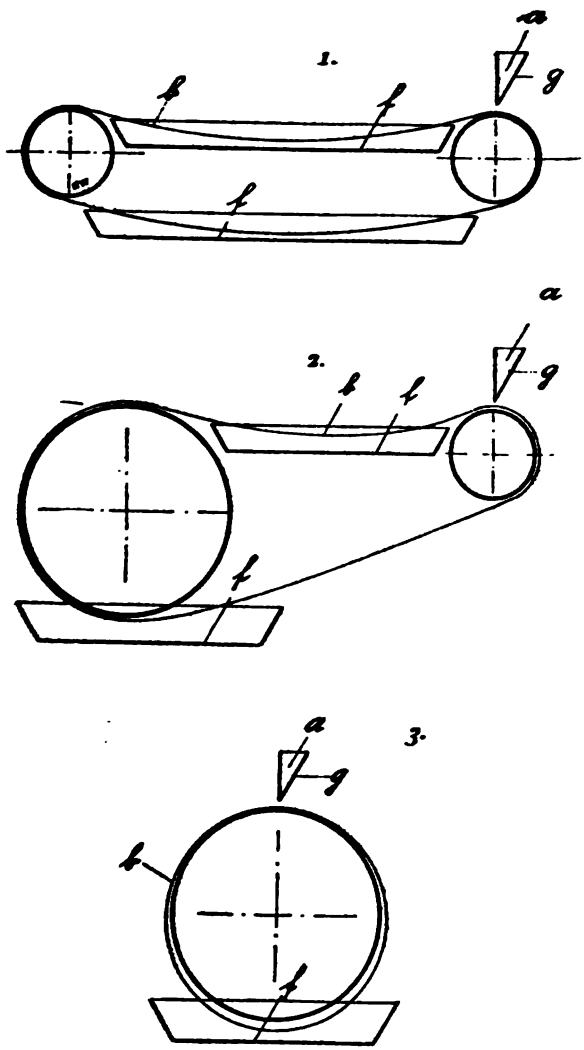
H. Danzer [2] renders cellulose films or bands impermeable to water or other liquids employed in the usual photo operations by either superficially acetating them or covering them with a cellulose ester varnish. Thus prepared, they may be used in place of celluloid cinematographic films.

In actual practice in the preparation or casting of continuous acetate films, a solid German silver belt has been found most satisfactory, the belt being 250-300 feet (80-100 m.) between centers, the wheels on which it runs being pulleys of 10-12 feet (about 3 m.) in diameter. It has been found advisable not to coat the entire width of the belt, but to leave about an inch space each side, to facilitate stripping. A little French chalk also rubbed on the belt is an aid to stripping. The cellulose acetate is placed in solution in any convenient manner, stored in glass lined or enameled tanks for some days for sediment to subside, then carefully filtered to remove extraneous particles. After filtration it is again stored for some days to allow all bubbles to rise, when the solution is in condition for use in continuous film formation. In casting

1. F.P. 401228, 1908; abst. J.S.C.I. 1909, **27**, 1064.

2. E.P. 3606, 1910; abst. J.S.C.I. 1910, **29**, 978; F.P. 410725, 1909.

a continuous acetate film on a German silver belt, or nickeled surface, the more tarnished the surface is up to a certain point, the better will the film strip off. When the belt is quite clean,



the film usually strips badly. It is a peculiar fact that continuous photo films always break easier in one way, usually

in the direction of their length, and not in the direction of their width.

In the process as devised by G. Bonwitt[1] (see Fig. 504), an endless band of metal or paper is conducted through a precitating bath (F) containing alcohol, toluol, or other suitable liquid. The pouring device G brings the mass A onto the band B, which carries the film through the bath F, where the precipitation of the film takes place. The solvent mixture is recovered by fractional distillation. The film obtained is said to be transparent, because the mass remains under continuous tension in the precipitating bath. The precipitation or congelation of the cellulose acetate is hastened by the presence of the non-solvent precipitant, the speed of precipitation being varied by the composition of the mixture containing non-solvent.

Waterproofing Acetate Films. The object of waterproofing acetate films is to protect the sensitized photographic image, and to increase the "life" of the film, i. e., the number of times it can be passed through the projectoscope before it becomes so scratched and worn as to be discarded.

After the films have been developed, and before being waterproofed, they are preferably cleaned and polished by winding them around a large cloth-covered drum without heat, where they are rubbed by hand with a soft felt moistened with benzene. Water is unsuitable for cleaning purposes on account of its action upon the gelatin, and alcohol is inadmissable on account of its possible action upon the cellulose ester support. The drum is revolved and firm but gentle pressure is applied to the film with a cloth dampened with benzine. Extraneous matter taken up from the various development and washing processes is thus removed, which, if left, would show up as streaks, blots or scratches upon magnifying the film upon projection.

The waterproofing application usually consists of a nitro-

1. D.R.P. 237151, 1908; abst. J.S.C.I. 1911, 30, 1232; Zts. ang. Chem. 1911, 24, 1838; Chem. Zentr. 1911, 500; Wagn. Jahr. 1911, II, 506. See also Bonwitt, Kunst. 1913, 8, 456. For the preparation of elastic masses of nitro- or acetyl-cellulose, see D. R. Anm. B-50757 of 1908.

cellulose solution of about 6 oz. per gallon, to which has been added 2 oz. of camphor and an equal amount of castor oil.[1] The solvent portion should be high boiling, amyl acetate 75%, benzol 100°, 25% by volume, being satisfactory. There are, in the best practice, two processes of waterproofing the film, the first being to render the gelatin surface receptive to the waterproofing solution. The picture during development is treated with tannin, chrome alum, formaldehyde and other astringent chemicals, all of which have a tendency to harden and constringe the gelatin surface so that it may become so tough and non-porous that the pyroxylin refuses to properly adhere without the gelatin being given some preliminary softening treatment. The sizing treatment has for its object merely to sufficiently open the pores of the gelatin so that the pyroxylin may penetrate and firmly become imbedded and anchored thereon and therein. The film, therefore, is first passed, face side down, through a bath of cold water, containing about 7% of glycerol by weight, the object of the glycerol being to moisten the gelatin surface for a sufficiently long time to enable the water to penetrate into and soften the gelatin substance. The film, after passing through rubber rollers immersed in water, emerges, engages two pads of chamois to more evenly distribute the water over the film surface, and then through two dry cloth pads which removes excess of water, and always some dirt. The film next passes over 100 feet or more of narrow belting to dry the film surface, the length of belting required depending upon the porosity of the gelatin film and the warmth and humidity of the room. By means of a delicately adjustable feeding arrangement the coating material is deposited on the film, best by two coatings, six inches to a foot apart, the solution covering the sprocket holes as well as the film body.[2] The pyroxylin coating after

1. H. Danzer, F.P. 420197, has described a method of waterproofing cellulose acetate films with pyroxylin.

2. This variation may be so great that when a 1000-foot reel is coated and wound, the diameter of the reels will sometimes vary as much as one-half inch. In order to keep the pyroxylin solution out of the sprocket holes, the film immediately after coating passes over an air blast which tends to keep the solution from the sprocket holes.

drying is usually about 0.001 inch in diameter, but this varies considerably, depending upon the proportion of pyroxylin which sinks into the gelatin substance.[1] After coating the film is carried over a drying machine, of which the Thompson pattern [2] has been extensively used in the United States. In the Thompson machine the reeling tape is approximately 1800 feet long, the waterproofed film, after passage through the machine, requiring about 45 minutes, is re-reeled at the other end and the process is then complete.

Automobile Wind Shields. The amount of inflammable products carried in an automobile and including the propulsive fluid, usually gasolene, together with the various lubricating oils, has concentrated attention upon replacing the inflammable celluloid as used in wind shields, motor hoods and windows, by a transparent non-frangible material of difficult combustibility. Such a material must be flexible, transparent, elastic and unaffected by snow, ice or water. Celluloid has been mainly used for this purpose, fulfilling to a satisfactory degree all the conditions except ready burning. Many of the plastic inducing bodies added to nitrocellulose possess the disadvantage of darkening upon long exposure to the light and air, so that cellulose ester plastics made from them exhibit an unmistakable tendency to become yellow and eventually brown when used in those parts of automobiles exposed to the light and air. Cellulose acetate sheets have been used to a limited extent for this purpose. While they contribute all that is desired in the way of slow-burning qualities, their chief drawback is an unmistakable tendency to become brittle and crack in cold weather. See also Part Five.[3]

Testing Acetate Films.[4] Acetate films to be acceptable to the trade should be uniform and sufficiently flexible and strong

1. The waterproofing room should preferably have several panels in the side walls consisting of openings covered with two thicknesses of fine linen, through which air is drawn by means of a fan, to minimize the introduction of dust during the waterproofing process.

2. U.S.P. 939350, 1908; 970972, 1910. See also W. Daniels, E.P. 24556, 1909.

3. The Automobile, Feb. 29, 1912; page 616.

4. G. Bonwitt, Chem. Zig., 1912, **36**, 641; abst. C.A. 1913, **7**, 2021.

to be projected 1000-1500 times without serious deterioration. The photographic emulsion should not strip from its support, either when wet or dry, nor should the support injuriously affect the emulsion upon long keeping. The completed film should not distort or alter in size either wet or dry, and upon magnification of 200 diameters, no dust or other insoluble particles should be visible, and finally the surface should possess the maximum resistance to mechanical damage ("scratches" and "rain"). For negative work the emulsion must be very sensitive and free from fog, the latter being necessary for the positive films, which should also give the fine-grained, contrasting, black images.

The testing of these films is usually confined to a determination of the following points:

1. *Thickness.* The thickness of the film (comprising the support plus the emulsion) should be 0.11-0.16 mm., and the width usually 34.7 mm., although the standard width is nominally 35 mm. The size of the picture was determined at the International Congress of Photography in 1900 at Paris as regards height and width, the ratio being 3 to 4, or 4 to 5, so that to these proportions the height and width are 18 mm. and 24 mm. respectively, leaving approximately 5.5 mm. for each perforation. The space between the films varies enormously with the make of the camera, but in general may be given as usually 2 mm. The breadth or width of the film is of great importance, as the slot in the cinematograph is 35.1 mm. broad, too broad to admit of films running through unevenly, the steadiness of the film being dependent solely on the perforations and width of the sprocket wheel and teeth.

2. *Constancy.* A satisfactory commercial film should not show a total shrinkage of more than 1.25% during 6 months. The usual cause of abnormal shrinkage is improper or incomplete drying of the film support and the gradual loss of the last traces of high boiling solvent or volatile plastic-inducing body or bodies. It is therefore advisable to test films periodically during a six months' period, allowing the film to remain in the air during the testing period. The constancy may also be altered by absorption of moisture by the gelatin present,

and its natural hygroscopicity. The adhesion of the gelatin to the cellulose acetate support is often facilitated by de-esterification (saponification) of the cellulose esters comprising the support. Water-soluble esters are thus formed, which combine with the aqueous emulsion and hold it well. Often the support, especially when composed of acetone-soluble acetates, is not entirely unaffected by water. The elongation may be determined by suspending a known length of film to which is attached a 200 grm. weight in water at room temperature for six hours, and the increase in length measured. This should not exceed 1.25%.

3. *Firmness and Elasticity.* These are tested in the usual manner in a Schopper machine, the latter amounting to about 5.7 kgm. per sq. mm. with 0.10-0.12 mm. thickness. The expansion varies between 10 and 15%. For more accurate determinations a practical test should also be made, for which purpose an endless film should be made and run through the projectoscope, determining from the speed and times the machine has run through, and the condition of the film at the completion of the series of tests. A good film should permit of at least 1200 runs without serious deterioration. The adhesion of the emulsion may be observed by tearing or quick rubbing of a folded film. According to Dr. E. J. Wall, of the University of Syracuse, one of the best tests is to slightly nick the edge of the film with a pair of scissors and then tear it sharply across at any irregular angle. An emulsion that sticks well will tear quite clean with the acetate support or leave a loose fringe on one edge which is so small as to be almost impossible to pick up except with fine forceps, and when so picked up, it immediately breaks off. Any emulsion that can be pulled off in a half-inch strip must be looked on with suspicion. The inflammability of the film is tested by placing a small strip in the gate of the projector. Without a picture on it, the film should not change, and only when the apex of the light cone strikes it, a needle-like hole should be burned. A film with a picture on it should melt, but not burn.

Perfect projection is only possible with true perforation, for each successive picture must stand in the same relative

place as the preceeding and succeeding one. There are four perforations per picture, the distance between adjoining perforations being 4.75 mm., the individual perforations being 2.6 mm. broad and 1.7 mm. high. To determine fog, electric markings, dust, etc., a test is developed before and after perforation and projected. Evenness of emulsion coating, absence of bubbles, comets, etc., are examined for by projecting a length of film which has been fogged and developed to an even, grey tone. Examination of this also enables the determination of the presence or absence of scratches in the support or emulsion. The gradation sensitiveness of the emulsion is determined in the usual way with a photometer. The positive film should show the same sensitiveness as that of an ordinary transparency plate. The picture should be capable of toning by the usual processes and staining with the aniline dyes.

Utilization of Waste Acetate Film. The economic utilization of discarded non-inflammable continuous picture film is a problem upon which has been expended an immense amount of thought and experimentation. Acetate film usually consists of three layers, a ground work or support of acetated cellulose comprising about 65% of the weight of the film. Upon this is superposed the gelatin layer in which is contained the photographic image, and this middle layer is both protected from being scratched and also waterproofed by a thin layer of a nitrocellulose solution. The problem, therefore, of separating the cellulose ester from the gelatin is rendered much more difficult by the fact that the latter is surrounded by a water-insoluble cellulose ester envelope, and this effectually seals the gelatin from the action of aqueous solutions, unless the upper and lower layers be first dissolved or destroyed. The methods of recovery which have been proposed may with propriety be classed with one of the three following processes:

1. The film, having been first cleaned from dirt and mechanical impurities by being reeled through warm water, thence over bristle scrubbers, and finally into clear water and dried, is dissolved in the proportion of about one pound of film to one gallon of solvent, experience having shown that solutions of this strength contain about the maximum of cellu-

lose acetate which will filter readily. Filtration is much easier if the film be not broken up as by agitation. Acetone or a mixture of acetone, tetrachlorethane and wood alcohol, is a satisfactory solvent combination, no heat being required. After filtration through paper, sand, asbestos or through a pressure plate filter, the residue is washed with solvent, filtered again, and the insoluble portion of gelatin containing the silver salts is ignited and the silver recovered from the ashes. One hundred pounds of original film will yield about three and a half dollars' worth of silver. This may be re-dissolved in nitric acid, and the silver nitrate employed again. The viscous solution of cellulose ester is either distilled in a partial vacuum until of the desired consistency for re-use, or the cellulose acetate and nitrate may be precipitated by water, washed and dried. The only loss of material in this process is the gelatin, the acetylcellulose and silver being regained. The disadvantages of this method are the large bulk of expensive solvents necessary, and their unavoidable loss in solution, filtration and subsequent vacuum distillation.

Where the extraction is carried on in a small way, the dissolved acetate may be placed in an air-tight can with cheese cloth or mole skin cloth bottom, and filtered into a receptacle which is air-tight, so the container is kept full of acetone vapor to prevent the filtering surface from drying or hardening, and hence decrease the speed of filtration.

2. The film, preferably disintegrated, is subjected to a ferment to dissolve the gelatin, thus leaving the cellulose ester unchanged. The comminuted film is digested at a warm temperature with a dilute aqueous pepsin solution, until the gelatin is substantially peptonated and has passed into solution. The film is then washed with warm water, the wash water evaporated to dryness and ignited for silver recovery, while the unacted upon cellulose ester portion is dried, and is then suitable for employment again. In this method the gelatin only is destroyed. The important item of cost in this process is the proteolytic ferment.[1]

3. Treatment of the original film with 10-20% sodium car-

1. Process of H. Danzer, Belg. P. 218192, 1909.

bonate solution at temperatures of 50-80° This, the least expensive of the proposed methods, is open to the objection that, unless great care is exercised, partial saponification of the cellulose ester occurs, and the finished acetate is inferior and of partial solubility only. The finished film by this process is apt to acquire a white and dull appearance, apparently due to superficial saponification by the alkali.

In the cyanide recovery process, the silver is first removed by cyaniding, next the gelatin removed by solution in hot water, leaving the celluloid undissolved, or, after the silver has been dissolved, the celluloid may be recovered by solution in acetone, leaving the gelatin behind. In this manner, the three constituents, gelatin, silver and cellulose ester, are recoverable. Any process useing warm water has the disadvantage that the water extracts the dyestuffs normally present in the film, and this colors the cellulose acetate.

Quantities of nitro and acetate film are at the present time ignited to obtain only the silver from the ash.

Chronophotography, Motography, or more usually "Motion" or "Moving Pictures," as commercially included in the present day refinements for the entertainment of audiences, comprises a process whereby a succession of photographic images pass before the observer, one being succeeded by another with such rapidity as to convey the delusion of motion. This deception is heightened by the fact that the objects in each succeeding picture remain stationary as compared with the immediate prior one, except some actor or object, the movement of one picture to another involving such a slight change that when a series of such pictures are flashed before the observer with sufficient rapidity, the graduation from one to the other becomes substantially indistinguishable to the eye, each picture appearing to imperceptably blend into the next succeeding one in the formation of the illusion of continuous motion. This illusion is intensified by the fact that the major portion of the picture remains stationary on the screen, the moving objects thus appearing in greater contrast, which renders more realistic the deception of actual movement. The standard picture film measures 1⅜ inches in width, although a

slight variation from this width is unimportant, because the edges of the film do not appear in the picture. The length of the film is immaterial, as two or more sections are usually cemented together. The thickness is about 0.006 inch, comprising about 0.005 inch of celluloid or cellulose ester film support, the depth of sensitive emulsion being 0.001 inch. When the picture occupies all of the film, so that it fills the screen when projected, the individual pictures are 1 inch by ¾ inch in size, being 1 inch wide and ¾ inch high, hench 16 to the lineal foot. The first picture on a strip of film in a series has its head at the end of the film and its foot toward the second picture in the series, from which it follows that the picture film is fed head-first through the projecting mechanism. The sprocket holes on each side of the professional film and designed to aid in feeding it through the projecting machine, are along each edge, outside the pictures, the pictures forming a long row 1 inch wide, and having as a border on each side a row of perforations, four holes per picture on a $\frac{3}{16}$ inch margin. The shape of the holes vary, but the number per picture is the same with all makers. The pictures in the strip are not necessarily 1 x ¾ inches, but they must occupy that much space, irrespective of their size.

The usual length of standard film roll as placed in the projecting machine for a public exhibition is 1000 feet, containing 16,000 distinct and separate images, which are flashed upon the screen at the rate of about 16 per second, a 1000 foot reel giving an entertainment lasting twenty minutes, which is the usual length of time of a nickel entertainment. It is immaterial whether the 1000 foot length reel be composed of one or several continuous scenes. The standard unit of exhibition film has therefore been made as 1000 feet—technically called a reel—moving-picture theaters basing their entertainment on that size film, while film-renting extchanges compute their prices on the basis of reels of this standard length. The manufacturers furnish films perforated or unperforated as desired.[1]

1. A reel containing 1000 feet of film forms a roll approximately 10 in. (25 cm.) in diameter, and weighs about 5 lb. (2.2k.) In a one-hour entertainment nearly 4000 feet of film passes before the audience, weighing 20 lb., and containing about 646,000 views.

The roll as received from the manufacturer is covered with tinfoil and black paper and inclosed in a metal box hermetically sealed. In November, 1914, it was conservatively estimated that in the United States alone there were in active operation over eighty-six thousand separate moving-picture theaters.

The motion-picture camera is required to have a good, fast lens, of a focal length of 2-4 inches, and arranged to take a picture 1 inch wide by ¾ high. Outside of the camera-box is a crank operating two mechanisms on the inside, the first being the film-shift mechanism by which a toothed roller is propelled with an intermittent motion. The unexposed film is placed in the camera, carried over this roller, the teeth of which catch the holes in the edge of the film strip. As the crank revolves, and intermittently jerks the toothed roller, the film is jerked down ¾ inch, or just the height of a single picture, the action being the same as with the projection machine previously described. The second camera mechanism is the shutter, the function of which is to exclude all light from the film when the handle is not turned, but to admit the light through the lens during that brief period when the film, between jerks, is at rest. The shutter and film mechanism work in juxtaposition, thus exposing the film to the light from the lens and then jerking the exposed film to darkness, while the immediately lying unexposed film is jerked into line for exposure. This alternate exposure and light protection is continued at the rate of about 16 complete cycles per second, until a sufficient number of impressions have been obtained, except that being undeveloped, they are still negatives. The speed of taking the pictures is varied to some extent, depending somewhat upon the effect desired upon the projection screen, and the nature and extent of animation of the subject being photographed. Usually the pictures appear on the screen faster than they were taken from nature.

The methods of development applicable for moving pictures are dependent primarily upon the length of the individual films. The average camera has a reel box of capacity seldom in excess of two hundred lineal feet of film, and for such length, the so-called "drum development" method is

extensively used. In this method the exposed strip is wound from the camera onto a drum, the drum being hung upon supports, and the sensitive film wound spirally, sensitive face outward. The drum is then turned toward the developer with its under surface immersed in the solution, then lifted to a tank of water and similarly turned; then to a tank of fixing solution, several tanks of water, and finally through a weak glycerol solution to preserve its flexibility. The film is finally dried and the negative is complete.

The making of the print from the negative is comprised in the processes of printing, developing, drying and inspecting. As in making a photographic print, the sensitive surface of the material for the positive must be placed in contact with the film side of the negative and the proper quantity of light admitted through the negative to the material which is to become the positive point. As the motion-picture negatives are 200-400 feet in length, special types of photographic printing frames are required, the machines used which print a portion at a time, either by the "step-by-step" or "continuous" processes until the entire strip is printed. The raw film stock on which the positive is to be printed is of comparatively slow emulsion. The development of the print is substantially the same as with the development of the negative, the final printing being done in a sectional machine.

Cellulose Acetate Window Panes. According to B. Borzykowski, who has patented a process for so doing,[1] sheets of well dried cellulose acetate may be used instead of glass, especially for automobile wind shields, carriage windows, and the windows and observation orifices of aeroplanes. The advantage claimed over nitrocellulose sheets, which have long been used for this purpose, is less liability to decomposition and turning brown. An antacid may be added to the cellulose acetate intended for this purpose, diphenylurea being especially useful, and tending to prevent decomposition from the development of free acetic acid.

Cellulose Acetate Phonograph Records. For some years phonograph disc and especially cylinder records have been

1. E.P. 21719, 1910; abst. J.S.C.I. 1911, **30**, 1213; Kunst. 1912, **2**, 76. F.P. 420555, 1910; abst. J.S.C.I. 1911, **30**, 363.

on the market, and manufactured under the patents of A. Petit,[1] F. Capp,[2] George H. Stevens,[3] and others, but there is a disadvantage in those records which contain camphor, in that they warp and shrink, due to the volatility of the solid solvent, so that they do not retain the record unimpaired for a considerable length of time.

J. Aylesworth has patented a duplicate sound record[4] which consists of the combination of a cellulose ester and a halogenized fatty acid. He claims that when such derivatives as the methyl, ethyl or amyl ester of a chlorinated fatty acid, as chlorinated stearic acid, is mixed with cellulose acetate, an impressionable surface is formed, especially suitable for recording sound undulations. In the composition, where great flexibility is required, the proportion of the halogenized fatty acid derivative may be increased until it exceeds in amount the cellulose ester. On the other hand, when it is desired to form more or less massive articles where flexibility is not so important, but where great toughness is desired, a smaller proportion of the halogenized fatty derivative may be used, or if great toughness and tensile strength is not important, the halogenizing of the fatty acid may be carried to the state of resinification. The phonograph composition consists of the halogenized fatty acid, as chlorinated stearic acid and a cellulose ester brought together by means of the common solvent acetone. Upon evaporation of the solvent there is left a tough, flexible and non-inflammable composition, the solid solvent being non-volatile, and in this respect differing from the camphor in celluloid. The mechanics of preparation of the duplicate sound record is detailed in the patents referred to.

According to the process of A. and L. Lumiere,[5] a flexible composition for phonograph manufacture is to be obtained by combining a cellulose acetate with a fatty acid, either dissolved in a common solvent or emulsified with it.

1. E.P. 22867, 1899. U.S.P. 689536, 1900.
2. U.S.P. 689536, 1901.
3. U.S.P. 650431, 1900; 667600, 1901.
4. U.S.P. 855556, 1907; 953454, 1910; 962877, 1910; abst. J.S.C.I. 1910, **29**, 940.
5. E.P. 15490, 1903; abst. J.S.C.I. 1904, **23**, 1041.

Or[1] the phonograph record may consist of a mixture of acetylcellulose with the oleate, margarate, stearate or palmitate of sodium or potassium, the acetylcellulose being first dissolved in alcohol, ether, acetone or chloroform.

Capping Bottles with Cellulose Acetate. A method has been patented[2] for sealing bottles by applying tubular or conical capsules of hydrated cellulose, the capsule being loosely placed over the neck of the vessel to be sealed. Upon exposure to the air it shrinks and contracts by reason of the gradual loss of water of hydration of the cellulose hydrate, and in shrinking, the capsule firmly attaches itself to the neck and any projecting surface of the bottle, and in the final dried condition is under considerable tension on its free surfaces, constituting a semi-transparent seal, rigidly secured by the automatic contraction during the elimination of water. The Viscose Development Co. and J. Morford[3] have adapted this idea to cellulose acetate on account of its property of separating from solution as a continuous film in combination with a large amount of water of hydration and water mechanically held. If a glacial acetic acid solution of acetylcellulose is spread upon a resistant surface as glass, and then exposed to water, it is coagulated to a translucent hydrated film composed in the wet state of about one part cellulose acetate to four parts of water. Capsules of this hydrated acetate may be prepared by dipping glass tubes into a 10-14% solution of acetylcellulose in glacial acetic acid, the tubes being then raised, drained, inverted so that the viscous solution accumulated toward the bottom of the tubes may flow back and evenly distribute itself over the external surface of the tubes. These are then plunged into a bath of water, the film rapidly coagulated, after which it is stripped from the tube and preserved in contact with water in the swollen condition until required for use.

1. A. and L. Lumiere, F.P. 338849, 1903, and First Addition 2694, and Second Addition 2707 of 1903. The Compagnie Generale de Phonographes, Cinematographes et Appareils de Precision (Swiss P. 61929; abst. Kunst. 1914, 4, 98) combine acetylcellulose with an ether-oxide of glycerol.
2. E.P. 2880, 1905.
3. E.P. 14194, 1910; abst. J.S.C.I. 1911, 30, 888.

Cellulose Acetate in Air-Craft Manufacture.[1] In the formation of fabrics for balloon and aeroplane use, considerable interest has been evinced in France in the use of acetated cellulose solutions as a protective covering for the canvas parts. According to the Societe Francaise des Tissue Biaises,[2] cellulose acetate in combination with caoutchouc makes an excellent protective lacquer for varnishing balloons on account of the low permeability of hydrogen through the envelope so treated, and also to the fact that where coal gas is used as the buoyant power, the well-known softening action of the gas upon rubber is entirely obviated from the presence of the acetated cellulose. Ordinarily the diminution of hydrogen from diffusion through the canvas or silk envelope not only diminishes the force of the ascension through loss of gas, and hence the time which it will remain aloft with a given load, but the loss of hydrogen is an important matter from the economic standpoint of cost. This Company proposes to remedy these inconveniences by coating the balloon envelope with the following solution:

Acetylcellulose, 15 parts.
Caoutchouc, 2 parts.
Tetrachlorethane, 100 parts.

These proportions may be varied within certain limits, and depending primarily upon the nature of the buoyant gas. As the result of further experiments[3] they conclude that

1. For "Materials used in making Balloon Envelopes and in Producing Gas-Tightness, see H. Hoenes, Gummi Ztg. 1911, **25**, 1281; abst. J.S.C.I. 1911, **30**, 797, Manufacture of Balloon Fabrics. Churrel, Gummi Ztg. 1912, **26**, 894, 938, 972, 1016, 1055; abst. C.A. 1913, **7**, 1811. Balloon and Aeroplane materials. G. Hubener, Kunst. 1913, **3**, 141, 164, 189, 207, 344; abst. C.A. 1913, **7**, 2693. Airship envelope fabric. Times Eng. Suppl. Feb. 26, 1913; abst. J.S.C.I. 1913, **32**, 282. Roll, E.P. 1315, 1913.

2. F.P. 427818, 1910; abst. Kunst. 1911, **1**, 455. L. Nottelle and R. Heraud (F.P. 445638, 1911; abst. J.S.C.I. 1913, **32**, 35) produce a varnish suitable for covering air craft by combining cellulose acetate with various gums and resins, acetone and amyl acetate, with or without the addition of rubber. After the varnish has been applied and has dried, the coating may be vulcanized by a coating of sulfur chloride.

3. Add. 14044 to F.P. 427818, 1910; Kunst. 1911, **1**, 455. The Internationale Celluloseester Gesellschaft, D. R. P. 241963, 1908; abst. C.A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 110, have also patented the use of cellulose acetate as a filling or covering material

better results are to be obtained where sulfur is added to the lacquer in amounts sufficient to partially vulcanize the caoutchouc. The sulfur is dissolved in hot alcohol and added to the lacquer formula above given. The balloon is first partially inflated, the lacquer then applied and allowed to dry, after which the inflation is completed.

In France, it appears that acetate lacquer is used to a considerable extent in lacquering aeroplanes, especially for the wings and other portions of the canvas. It has been found that cellulose acetate when dissolved in a mixture of tetrachlorethane and acetone, furnishes a lacquer which renders the canvas thoroughly waterproof, and adds materially to the tensile strength of the craft. The lacquer is preferably applied to the parts after assembling rather than to the canvas before attachment to the wing frame-work. It may be applied two coats to the skyward side of the plane, or one coat to each side—preferably the former. Where the maximum softness and pliability is desired, small amounts of castor oil or acetin may be added to the lacquer, while the opposite effect of stiffness and rigidity may be imparted by the addition of resins as shellac, dammar or copal. The Societe Leduc, Heitz et Cie,[1] who have been mainly instrumental in exploiting cellulose acetate for use in this field, do not use Cellon,[2] but rather an acetone solution of cellulose acetate diluted with benzene and ethyl alcohol, or, a 25% solution of cellulose acetate in acetone containing 2.5% *b*-naphthol and 2.5% hexachlorethane and pyridine. The fabric, filled with cellulose acetate, is further protected by the application of one or two coats of linseed or poppy seed oil varnish in combination with opaque pigments of

in the construction of air-craft. See this firm's D.R.P. 277529, 1909; abst. Kunst. 1914, **4**, 335, for use of resorcinol diacetate with acetated cellulose. Compare also Fuerst Guido Donnersmarck'sche Kunstseiden und Acetatwerke, Aus. P. 8165, 1902; Aus. Appl. 1905, 1909; Swiss P. 46329, 1909. For a description of the H. Dittmar process (D.R.P. 266384, 1911; abst. C.A. 1914, **8**, 2041) see Part Three.

1. E.P. 6798, 1912; abst. J.S.C.I. 1912, **31**, 1016. F. P. 429788, 1911; abst. J.S.C.I. 1911, **30**, 1267; C.A. 1912, **6**, 2186; Oil Paint and Drug Review, Apr. 24, 1912; Chem. Tech. Rep. 1912, **36**, 63. Belg. P. 229396.

2. Kunst. 1913, **3**, 317.

any desired color.[1] The acetated celluloses in solution also find use in the formation of balloon and aeroplane fabrics. It has been shown that in a parallel fabric, the limits of a compound stress are the limits of tensile strength of warp and weft, while for diagonal material the bursting strength appears to be about 1.4 times the strength determined by simple tensile strength. Coating of the strands before weaving with thin acetate solutions—so fluid as to admit of complete impregnation—is said to materially raise the tensile strength and impermeability in both kinds of weaving.

According to a process patented by the Act.-Ges. f. Anilin-Fabrikation [2] imitation rubber with a basis of acetylcellulose may be prepared by mixing the cellulose ester with a substance of low volatility capable of conferring plasticity upon the mass, loading or coloring matters being added as desired. For example, 1 part of nitroacetylcellulose (acetylnitrocellulose)[3] is digested with 2 parts of methyl phthalate. When the temperature reaches about 60° the mass swells up and agglutinates. The addition of a small quantity of a volatile solvent, such as acetone, hastens the swelling. The mass may be colored black by the addition of an alcoholic solution of nigrosine. Or, 5 parts of acetylcellulose may be digested with 10 parts of triacetin and 1 part of amyl alcohol. The mass may be mixed with reclaimed rubber and 7 per cent. of sulfur and vulcanised by heating for 1 hr. at 135°. It may also be dissolved in 2 parts of acetone and 3 parts of benzine added to the solution, which may then be employed for impregnating fabrics. Or the mass may be run into the form of a thin sheet at 60° and under a pressure of 50 to 150 kilos. per sq. cm., and applied to a fabric under pressure. The surface of the fabric should be first prepared with a dilute solution of 1 part of nitroacetylcellulose, 1 part of triacetin and 10 parts of tetrachlorethane or acetone, and dried.

1. F.P. 446627, 1912; abst. Kunst. 1913, **3**, 475; J.S.C.I. 1913, **32**, 132; E.P. 6798, 1911; abst. C.A. 1913, **7**, 3032; E.P. 21426, 1911; abst. J.S.C.I. 1912, **31**, 1027; C.A. 1913, **7**, 1108. D.R.P. Anm. 8k; L-32835; abst. Kunst. 1913, **3**, 100.

2. E.P. 5633, 1914. F.P. 463622, 1913; abst. J.S.C.I. 1914, **33**, 431; Kunst. 1914, **4**, 195.

3. F.P. 449253, 1912; abst. J.S.C.I. 1913, **32**, 482.

L. Nottelle and R. Heraud (1) prepare acetylcellulose lacquers especially suitable for the impregnation of balloon envelopes and monoplane and biplane wings, by mixing the cellulose ester (either cellulose formate, acetate or nitrate) with oils, fats, gums, resins or rubber which is subsequently vulcanized.

Or,[2] coatings may be spread on fabrics and other materials which are efficient substitutes for balloon fabrics and for the formation of artificial leather by coating the cloth with a solution of acetylcellulose or nitroacetylcellulose in a mixture of 90 parts of tetrachlorethane and 10 parts of amyl alcohol or refined fusel oil. As the two solvents evaporate at an approximately equal speed, the uniform distribution of the coating is facilitated. Inasmuch, however, as neither tetrachlorethane or amyl alcohol are solvents of nitrocellulose, it would appear that substantial amounts of a nitrocellulose "high boiler" solvent such as amyl acetate would be indicated.

In the preparation of lacquers especially suitable for the coating of air-craft, the Chemische Fabrik v. Heyden [3] employ the acetone-soluble cellulose acetate modified by hydrolysis, combined with a softener as castor oil and a high boiling liquid such as chlorbenzene, toluene, carbon tetrachloride, oil of turpentine or similar organic body. Such diluting materials as dichlorhydrin or *iso*bornyl acetate are specified as useful additions to impart desirable characteristics. Their preferred formula is as follows:

Acetylcellulose, 10 grms.
Acetone, 55 grms.
Monochlorbenzol, 9 grms.
Castor oil, 2.5 grms.

The acetylcellulose is dissolved in the acetone, the castor oil added, and finally the monochlorbenzol incorporated.

1. F.P. 445638; abst. Kunst. 1913, 8, 474; 1914, 4, 38.
2. F.P. 461058, 1913; abst. J.S.C.I. 1914, 33, 20. For "Emaillite" as an acetate proofing lacquer see W. Vieweg, Kunst. 1914, 4, 187; Firma L'Emaillite, Kunst. 1914, 4, 218. See also "Flight" of Jan. 10, 1910; Deutscher Luftfahrer-Zts. Feb. 17, 1914. Belg. P. 209561.
3. D.R.P. 211520, 211573; D.R. Anm. C-23158. D.R. Anm. C-23487. Kunst. 1913, 8, 478.

The production of a vulcanized, highly porous or foam-like mass of rubber has been described by F. Laarmann [1] by

1. U.S.P. 1089482, 1914; abst. C.A. 1914, 8, 1679. For other methods of obtaining rubber foam see U.S.P. 753206, 753300, 857960; F.P. 329117; D.R.P. 174001. A. Eichengruen states the following in respect to that partially hydrated cellulose acetate called "Cellon." (Kunst. 1913, 3, 348.)

"The idea suggested itself readily to employ the solution of the non-inflammable celluloid, 'Cellon,' for the production of impregnations and coatings for making the materials treated with it non- or difficultly inflammable. Cellon has become of importance in aeronautics, due to the non-inflammability (the newspapers reported the surprising fact that in a recent lamentable Zeppelin catastrophe the Cellon planes remained intact, while the balloon covers were totally destroyed). Certain other properties make it also valuable for the purpose mentioned. Owing to the high viscosity of the Cellon solution, it is possible to provide, with a single stroke, the carrying surfaces with a uniform, enamel-like, smooth coat of Cellon, penetrating in all the pores and making them not only water-proof, but, in contradistinction to rubber cloth, almost completely benzine and oil-proof; consequently they are not affected or softened by the oil splashing on them from the motors or propellers. The principal advantage is, however, the attainment, by the varnishing, of a smoothness of the surfaces, which materially reduces the resistance to the air and therefore greatly and favorably influences the speed. Cellon solutions have therefore attained considerable importance and are sold under the name of 'Cellon-Emaillit.'

"It is, however, a surprising fact that the fabrics treated with Cellon solution are not made non-inflammable and are not even as difficultly inflammable as the cellon itself. It naturally was to be expected that, if a piece of cotton or linen fabric, by itself not readily combustible, would be treated by the practically non-inflammable cellon, the material would become entirely non-inflammable, or at any rate, show only a moderate combustibility. As a matter of fact, however, a cellonated fabric burns just as easily as a non-cellonated one, and not much less than rubber cloth or oil-impregnated fabric. If a piece of Cellon film is placed over a piece of cotton fabric it becomes possible to light the Cellon film with a flame, and it begins to burn with a luminous, smoky flame, as if it were a combustible material. Even if instead of the plastic Cellon a solution of pure cellulose acetate is used (which would be impracticable, as the cellulose acetate coats become brittle after the complete evaporation of the solvent, which, however, will only be the case after several months, and thus may cause a tearing of the aeroplane surfaces), a certain degree of combustibility of the cotton fabric nevertheless remains. A little may be done to remedy this defect by impregnating the fabric with the above mentioned salts, but this is not practicable in the case of aeroplane and balloon fabrics, as these would be washed out again by the rain or even on cleansing the apparatus and because these impregnations weaken in time the carrying surfaces enormously. Apart from this, such an impregnation is furthermore entirely inadequate, if plastic acetate coats, which increase the carrying power of the planes, are used for aeroplanes, or soft rubber-like coatings for balloon covers. These flexible Cellon fabrics burn, even if the fabric has been preliminarily impregnated with

combining rubber with an alcohol-ether solution of nitrocellulose or a chloroform solution of acetylcellulose. A foam is formed with a solution of the material, a. g., rubber in carbon bisulfide, with a compressed and inert gas such as nitrogen, and in a closed vessel, the foam is then fixed by vulcanization with the chlorides of sulfur in the case of rubber, the receptacle being finally opened and the solvent evaporated off.

Coating Cigar Tips with Cellulose Acetate. As far back as 1872 J. Harris recognized the value and desirability of protecting the teeth from discoloration from tobacco by waterproofing the mouth end of cigars with cellulose ester solutions, useing for this purpose nitrocellulose. Not only is a portion of the aroma and bouquet of the cigar preserved by such an impregnation, but the presence of the insoluble film retards to a large extent the oils of the tobacco from entering the mouth. In 1910 a patent was issued in which cellulose acetate was specified but not claimed for this purpose,[2] the

metallic salts, as readily as rubber cloth, although they surpass the latter by their extraordinary impermeability to water and their dielectric constant.

"The phenomenon that a non- or hardly inflammable fabric becomes combustible by impregnating or varnishing it with the non-inflammable Cellon is not only most surprising—it might be explained by a kind of wick-action—but also very undesirable, because it deprives the cellonation of the fabrics of its chief advantage, the non-inflammability. Long and tedious experiments were necessary to eliminate this disadvantage and to produce a variety of cellon which makes the fabrics really non-inflammable, but we have recently been successful in attaining this. It is now possible to produce washable cellon collars and cuffs similar to the celluloid articles, which may be placed in direct contact with a flame without being affected in any other way than by getting black. It is also possible to produce an absolutely non-inflammable and non-combustible aeroplane and balloon fabric. By applying cellon lacquer the carrying planes of aeroplanes are not only stretched like a drum-head, but they also become fireproof to such an extent that benzine may be poured over them and ignited without affecting the surfaces in any other way than that they become blackened and partially carbonized and swell up. One of the many sources of dangers which accompanies the conquest of the air seems thereby removed, namely, the complete destruction of the aeroplane or balloon by fire in case of the spreading of a benzine fire on the wings of an aeroplane. Whether it is possible to increase the safety of the dirigible by coating the outside covers with fireproof cellon lacquer cannot be decided without more extensive experiments."

1. U.S.P. 126698, 1872.
2. C. Schroeder, L. Levi and A. Lasche, U.S.P. 951582, 1910.

essence of the invention being to impregnate the mouth tip of the cigar with a cellulose compound,[1] an inorganic salt of a fatty acid [2] and a balsam,[3] together with an ingredient to effect solution of the elements as alcohol, acetone or tetrachlorethane.

F. Meyer has pointed out [4] that nitrocellulose solutions have the disadvantage of too great contractility, so that cigars so coated often shrivel up, become contorted and otherwise cause the outer leaf of the cigar as well as the underlying layers to crack, thus spoiling their appearance, and otherwise reducing their value by interfering in their evenness in drawing. To obviate the above, an alcohol or acetone soluble cellulose acetate is recommended of such concentration that one dip will be sufficient. Any tendency to contraction upon drying may be obviated by the addition of a small amount of castor oil. The coating may be made invisible by dissolving a small amount of bismarck brown in the acetone used for dissolving the cellulose acetate. A dull appearance free from gloss is to be obtained by substituting a brown pigment for the dyestuff, raw or burnt umber or sienna being insoluble in water or alkaline or acid solutions, and hence affecting the smoker in no way by their use. Cellulose esters have a distinct value in this connection in preventing the wrapper of the cigar from unwrapping, and decreasing the tendency to the looseness which ordinarily arises from handling.

Cellulose Acetate in Pharmacy.[5] Collodion in its various forms is official in the Pharmacopeas of nearly all countries,

1. As soluble cellulose, dinitrocellulose, cellulose xanthates, or acetylcellulose.

2. As calcium, barium or strontium caprylate, magnesium stearate, or calcium oleate, linoleate or ricinoleate.

3. As Canada balsam, Venice turpentine or balsams of Peru, tolu, storax, benzoin or copaiba. In the patentee's preferred formula, 40 cc. of collodion is mixed with 1 gm. calcium resinoleate, 1 cc. Venice turpentine and 8 cc. alcohol. The turpentine and resinoleate are first combined by heat, after which the remaining ingredients are incorporated.

4. U.S.P. 931629, 1909; D.R.P. 193210, 1906; abst. Mon. Sci. 1911, (5), 74, 92. Can. P. 107996, 1907.

5. See E. Worden, "Acetate Collodion," Science, 1911, 34, 256; abst. Zts. ang. Chem. 1912, 25, 322. Cross and Bevan (U.S.P. 530326) first suggested cellulose acetate for pharmaceutical uses.

and usually comprises an ether-alcohol solution of nitrocellulose, to which various medicaments are added. As collodion is used in medicine and pharmacy only as an external application, and has no therapeutic action outside that of a protective covering, the solvent portion must be regarded as merely the vehicle for the topical application of the nitrocellulose. Ether and alcohol, like the cellulose nitrates, are inflammable. Cellulose acetate, on the other hand, burns with difficulty, and may be dissolved in fluids like tetrachlorethane, which also are unburnable. Therefore, from a standpoint of safety, it would appear that the cellulose acetates, dissolved in solvent mixtures of low flammability, might with profit replace the more inflammable nitrocellulose, now official in the various Pharmacopeas for many years. The solvents of nitrocellulose may also be used for cellulose acetate, so that those medicaments now official in various collodions, as castor oil, Venice turpentine, tannin, iodoform, Canada balsam, Cannabis Indica, camphor and chloral, may be used with equal advantage in solution with the cellulose acetates. The acetates have the desired adhesive power in contracting surfaces, constringing the edges of a wound, or coapting cuts or fissures. Tetrachlorethane and alcohol form excellent solvents for cantharis, iodoform, resorcin, alkaloids, glucosides and the antiseptics and fungicides used in external applications. An excellent remedy for the removal of warts comprises cellulose acetate 4 parts, acetone 70, and trichloracetic acid 10 parts. An efficient application for the softening and removal of corns consists of cellulose acetate 12, tetrachlorethane 8, acetone 75, and chloral hydrate and camphor, each 1 part.

According to A. Eichengruen [1] salve-like or gelatinous cellulose acetate preparations for medical, cosmetic or edible purposes may be prepared by mixing aqueous-alcoholic soiutions of cellulose acetates with a softening agent or with a solvent having a therapeutic or perfumatory character, with or without a sweetening substance. Suitable materials for use are ethereal oils, neutral esters of organic acids, gaultheria oil,

1. D.R.P. 268489, 1911; abst. C.A. 1914, 8, 1489; Chem. Ztg. 1914, 38, 20. E.P. 26987, 1912; abst. C.A. 1914, 8, 1644.

and perfumes such as heliotropine. The salve-like masses may be used for medical or cosmetic purposes if used for carrying antiseptic, anti-rheumatic, or anti-pruriginous substances, or perfumes, softening agents such as glycerol, or astringents such as aluminum acetate. The salves, when applied to the skin, finally leave behind a protective coating of cellulose acetate. Gelatinous edible preparations may be made by using alcoholic drinks, such as liquers, as cellulose acetate solvents, and sugar, etc., may also be added, giving a solid liquer.

According to J. Peck[1] a useful material for the manufacture of surgical and medical jackets, splints, and other supporting-appliances, consists of gauze or other fabric treated with cellulose acetate or other substantially uninflammable cellulose ester or double ester, dissolved in or mixed with acetone, etc. Castor or other suitable oil or camphor, or celluloid solution containing metallic or ammonium chlorides, or any combination of these substances, may be added to the cellulose ester solution. Successive layers of the fabric treated with the composition may be applied to a model of the article to be made until the desired thickness is obtained.

There are vocations to the members of which it is of great trouble and annoyance that traces of their profession appear upon their hands. This is especially true in photography, due to the darkening of the fingers when working with silver solutions. By painting the fingers with a cellulose acetate solution and removing the same with a little alcohol or acetone at the close of the day's work, the fingers may be kept unstained.

Solidified Spirit. (Solidified Alcohol, Solid Spirit, Alcohol Cubes, Travelers' Alcohol, Smaragdin.) Of recent years a number of preparations have been introduced, which, added to ethyl alcohol, causes the entire mass to solidify in a sufficiently firm condition to be cut into cubes of about one inch in diameter, in which condition it appears in commerce. Some of these preparations, however, like the soap and paraffin combinations of R. Wild,[2] either seriously decrease the

1. E.P. 2425, 1913; abst. C.A. 1914, 8, 2624.
2. E.P. 5404, 22181, 1901; abst. J.S.C.I. 1902, 21, 244, 1226.

calorific power of the alcohol, burn too slowly, or leave such large quantities of unconsumed residue upon ignition that their free and continuous burning is seriously impaired.

The speed of burning may be materially increased by the addition of such inflammable materials as the cellulose nitrates, as described in the patented processes of L. Denayrouze,[1] G. le Fortier[2] and V. Perelzvich and G. Rosenbuch.[3] In the former method the alcohol is solidified by the addition of 5-15% of vegetable wax, stearin or paraffin wax, together with sufficient nitrocellulose to impart the freedom of burning desired. In the latter process synthetically produced tristearin obtained by heating an alcohol such as glycerol with stearic acid for a considerable time at a high temperature, is combined with an alcoholic or ethereal solution of cellulose nitrate in such proportions that upon cooling the mass containing the alcohol, separates in substantially a solid state. The patentees assert that a mixture of 3% of tristearin, 5% sodium sebate and 1% of nitrocellulose in solution are the proper proportions for a mixture which produces a flame of maximum heat, melts very slowly, leaves but a trifling residue and obviates all danger of explosion. It is a fact that this mixture can be made to gelatinize and eventually solidify, but it is also a fact that the rapid burning caused by the presence of the inflammable nitrocellulose has a tendency to cause the burning mass to soften and liquefy.

The Farbenfabriken vorm. F. Bayer have overcome this objection by employing cellulose acetate as the gelatinizing medium,[4] useing acetic acid as the menstruum, and adding the alcohol directly to the dissolved cellulose acetate in such proportions that the entire mass gelatinizes and eventually changes to a firm coagulum which can be cut into convenient sizes and transported without material change or appreciable

1. E.P. 17687, 1900; F.P. 296132, 1900, and First Addition No. 3962 dated Nov. 19, 1904; abst. J.S.C.I. 1901, **20**, 976; 1905, **24**, 429.

2. Belg. P. 195098, 1906.

3. U.S.P. 919759, 1909; E.P. 26915, 1907; F.P. 397092, 1908; abst. J.S.C.I. 1908, **27**, 826; 1909, **28**, 693; 1912, **31**, 514; Chem. Abst., 1909, **3**, 580, 1803; 1910, **4**, 3121.

4. D.R.P. 134721, 1901.

loss of alcohol when preserved in a closed container. In their preferred method 100 gms. of cellulose acetate is dissolved in 500 gms. of glacial acetic acid,[1] the heavy, viscous and translucent mass being poured into two liters of ethyl alcohol, either pure or suitably denatured. The excess of alcohol and acetic acid is removed from the gelatinous mass, the latter being partially dried and kept in closed containers until used. Prepared in this manner, the large amount of concentrated acetic acid unavoidably left in the coagulated mass attacks the mucous membranes upon ignition, the ignited mass giving off a penetrating acetous odor difficult to mask. Cellulose acetates, however, are known which are completely soluble in 70% alcohol and stronger, by which means it is possible to eliminate acetic acid and dissolve the acetated cellulose directly in the alcohol by gentle heat. Upon cooling such a solution the cellulose acetate gelatinizes sufficiently firm to retain the alcohol without serious exudation. The firmness of the mass depends upon the amount of cellulose acetate incorporated therein, the product of Bayer comprising 85-92% of denatured alcohol gelatinized with 8-15% cellulose acetate.

The speed of burning may be modified by combining both cellulose acetate and nitrate with alcohol, both esters being first dissolved in a solvent mixture so weak in dissolving power as to induce incipient precipitation upon cooling, the degree of jellification and the consistency of the coagulum formed being controlled by the nature of the solvents and non-solvents composing the fluid portion, and the nature of the cellulose esters selected. A heavy, viscous nitrocellulose, similar to that used in the manufacture of transparent celluloid and similar plastics, when combined with an acetated cellulose which has been partially hydrolyzed until soluble in hot diluted alcohol, gives best results in the author's hands. The speed of burning may be modified and the tendency to

1. As anyone who has tried will agree, the solution of not-hydrated cellulose acetate in glacial acetic acid is a very slow and tedious undertaking. One method is to grind the horny acetate to an impalpable powder and add it in small portions to glacial acetic acid at 50-60° C., subsequently agitating in the presence of a number of marbles or small porcelain balls.

liquify obviated by a judicious adjustment of the proportion of acetate to nitrate in the solid portion. A small amount of stearic acid adds greatly to the firmness of the coagulum without apparent detriment. This firmness may be increased by partial removal of alcohol by distillation under reduced pressure, the hot material from the still either being run into moulds or cut into sections after cooling. By the addition of small amounts of oleoresinous or balsamic bodies in solution, the odor of the alcohol may be masked or modified. Balsams of Peru, tolu, benzoin or storax, or minute amounts of such bodies as safrol, eugenol, cinnamic aldehyde, patchouly, vetiver, oil of amber, cade or terpenes and essential oils are suggested as suitable for the purpose.

Feculose. As the result of the researches of C. Cross and J. Traquair [1] on the superficial or partial acetylation of starch, certain patents have been issued to them [2] and to the firm of W. Wotherspoon [3] for the formation of starch acetate, the product as produced by them being known under the commercial name of "Feculose," from "fecula," the Latin for starch.

Their product is not formed by the aqueous hydrolysis of starch; on the contrary, it is said to be best practiced in the absence of water on account of the tendency of starch granules to swell under the influence of moisture. In preparing this material some form of starch—preferably farina or potato starch in fine powder—is dried at 80-100° and fed into a vessel such as a rotary steam-jacketed converter, to which (calculated on the weight of the starch) about 30-50% of glacial acetic acid is added. The vessel is closed and slowly revolved until the acid and starch are uniformly mixed, when steam is admitted by means of the jacket, and agitation and heating continued for one to two hours and until a sample withdrawn

1. Cross, Bevan and Traquair, Chem. Ztg. 1905, **29**, 527-528; Traquair, J.S.C.I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1053; C.A. 1909, **3**, 2070. J.S.C.I. 1910, **29**, 323; abst. Bull. Soc. Chim. 1910, (4), **8**, 1150.

2. E.P. 9868, 1902; abst. J.S.C.I. 1903, **22**, 1008; Mon Sci. 1904, (4), **60**, 37. U.S.P. 778173, 1904; abst. J.S.C.I. 1905, **24**, 98.

3. F.P. 334154, 1903; abst. J.S.C.I. 1904, **23**, 29. D.R.P. 182558, 1903; abst. Zts. ang. Chem. 1907, **20**, 1781; Mon. Sci. 1909, (4), **70**, 77. Belg. P. 171743, 1903.

is found to be acetylated to the desired degree.[4] After cooling, the uncombined acetic acid is removed by either washing in a small bulk of cold water or by the addition of borax or alkaline carbonates, the neutral product being dried at a low temperature.[5]

The acetylated starch thus prepared is stated to differ from soluble starch both in chemical properties and in the fact that it completely dissolves in boiling water to a clear or slightly opalescent solution which skins over the top only with difficulty; does not gelatinize or separate out for some time; resists the action of ferments and is not prone to mold; when dried yields a colorless, transparent and continuous film, which, however, has but a low tensile strength and but little flexibility. It does not differ in appearance from the original unacted-upon starch. It does not reduce Fehling's solution and gives the usual blue reaction with iodine. Alcohol or concentrated saline solutions precipitate it from aqueous solutions in a manner similar to soluble starch, and it reacts with diastase under certain conditions.

4. A smaller proportion of acid—20-30% of the weight of the starch—may be used if the acid is sprayed upon the starch with a suitable atomizer and the mixture then charged into the converter. During the operation of heating, or at its conclusion, the vessel may be connected with a condenser and a portion of the free acid distilled off for re-use. Instead of employing glacial acetic acid, the acid may be produced as vapor by treatment with a non-volatile acid (sulfuric), an inorganic acetate (calcium), and conducting the vapor into the mixer containing the starch, until the latter, in the dry state, has absorbed about 20%. The mixture is then fed into the heated converter.

5. The development of the process has mainly been along the lines of limiting the quantity of acid and perfecting its recovery, but it has been established that 10% of glacial acetic acid on the dry starch was the minimum which will produce useful products. Although acetylation may be considerably accelerated by the presence of small amounts of mineral acids along with the acetic acid, care has to be exercised in the control of the esterification that the yield is not diminished by conversion of the starch into water-soluble products of hydrolysis. The 4-5% of free acetic acid which is present in the acetylated starch as it leaves the converter is removed by washing with cold water. It is therefore obvious that for maximum yields the conversion must be limited to the formation of products which are water-insoluble, because if the reversion is carried too far, not only does the loss become serious, but the acetylated starch granules appear to hydrate in cold water to a colloid, glutinous mass. Under proper conditions of esterification,

With the majority of chemical reagents, acetylated starch is more reactive than natural starch. Feculose as prepared for the market is neutral or slightly acid and as shown by saponification with sodium hydroxide contains from 1-4% of combined acetic acid calculated on a C_6 molecule.[1]

The technical uses of acetylated starch have been pointed out by Traquair [2] and by J. Farrell [3] and are briefly as follows:

In its applications as a special textile finish, its colloidal properties enable it to confer luster, to penetrate and impart body and "handle" to textiles in the form of yarn or cloth. The clear filming property is especially noticeable on bright colors such as reds and yellows, where it appears to increase intensity of color. In connection with ordinary starch, it imparts flexibility and clearness to the finish. As a dressing for linen and lace it is stated to impart the desired springy effect and can be used on mercerized cotton without affecting the luster. J. Farrel [4] has obtained satisfactory results with Feculose as a stiffening agent in giving body to a fabric and in dyeing and French cleaning. In silk finishing little sizing materials are used in addition to the salts added to impart the scroop effect. Acetylated starch is applicable in the manufacture of confectionery, especially in gum-drop, ju-jubes, and similar paste confections, as it may be cooked up with sugar and glucose to any "steam" temperature.

In the manufacture of paper [5] in fluidity, permanency of solution and filming power, the starch esters are of distinct value. The film, however, is soluble, which solubility may be decreased by subsequent treatment with dilute formaldehyde.

however, the acetylated starch may be washed and dried like ordinary starch.

1. It appears to be a reasonable assumption that the reacting molecules are capable on hydration of radically influencing the entire complex, with the result that deep-seated changes occur simultaneously with a fixation of acetyl groups.

2. J.S.C.I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1152-53. J.S.C.I. 1910, **29**, 323-329; abst. Zts. ang. Chem. 1910, **23**, 1824; Bull. Soc. Chim. 1910, (4), **8**, 1151. Pharm. Jour. No. 2379, 680; abst. Merck's Rep. 1909, **18**, 179.

3. Jour. So.c Dyers Col. 1908, **24**, 323; abst Zts. ang. Chem. 1909, **22**, 221. J.S.C.I. 1909, **28**, 19.

4. l. c.

5. J.S.C.I. 1910, **29**, 323.

No starch product has the ink-resisting property of gelatin, but in the sizing of tub-sized papers, the addition of a little rosin to feculose solutions with the subsequent addition of a small amount of alumina, produces a size which is satisfactory under many conditions. Starch acetate solutions, being decidedly colloidal in character, do not possess the power of penetration of gelatin and the other animal sizes.[1] If engine-sized writing paper where the paper has been fully rosin-sized in the beater is run through a weak acetylated starch solution and dried in the paper making machine, the writing quality of a tub-sized paper is imparted. In printing papers where the production of a good printing surface is the first requisite, acetated starch and china clay has been used in weak solution on the water doctor calendar, the coat in any instance being applied light.

A. Militz [2] and the Farbenfabriken vormals F. Bayer and Co.[3] have described a process for preparing a soluble starch by the incomplete or superficial acetylation of starch granules, the product being of technical interest as an adhesive and a stiffening agent in the treatment of textiles, as a substitute for acacia or tragacanth. The product is prepared by treating a cold suspension of starch in acetic acid with small quantities of mineral acids, e. g., nitric acid, hydrochloric acid or sulfuric acid, washing to neutrality in cold water and drying. For example, if 500 parts of potato flour (preferably dry) is quickly introduced with continuous and vigorous stirring into a mixture of 250 parts of 98-99% acetic acid and 7.5 parts nitric acid of 40° Be., the rather thin liquid first formed subsequently solidifies into an easily triturable voluminous solid. The mixture is allowed to stand for 24 hours for reaction to become complete, washed with cold water, the product filtered off and

1. A typical sizing bath is composed of two parts of 12.5% solution of feculose and one part of 6.5% solution of gelatin, with sufficient alum to impart the desired viscosity. It is claimed that feculose gives the paper a distinct quality, makes the sheet more pliable and improves the writing quality by decreasing the hardness and ink-repellant nature of the surface.

2. U.S.P. 941159, 1909; abst. J.S.C.I. 1909, **28**, 1322.

3. E.P. 25274, 1907; abst. J.S.C.I. 1908, **27**, 761. F.P. 383902, 1907; abst. J.S.C.I. 1908, **27**, 415.

dried at about 40°. The purified and neutral product has the appearance of the original starch granule, is insoluble in cold water, but readily dissolves in water of 70° to a stiff gelatinous mass, which is strongly adhesive and may be kept for a considerable length of time without detriment to its adhesive qualities. The solution neither congeals nor coagulates when properly prepared. A 5% solution of the acetylated starch gives a violet color with iodine, and when heated on the water bath with caustic soda solution containing 5% Na_2O calculated on the weight of the acetated starch, no starch can be recovered from the solution, nor can the formation of starch be observed during any stage of the reaction. Saponification with caustic alkali and distillation with a non-volatile acid as phosphoric acid, gives a distillate containing acetic acid.

W. Dixon [1] obtains that acetate of starch known as "feculose" and other starch esters as the formate, by the action of glacial acetic or other monocarboxylic acids such as formic acid upon starches.

Alkylation of Cellulose. W. Suida [2] in 1905 did much pioneer work upon the benzoylation of cellulose, in connection with the study of the influence of active groups in the textile fibers upon the process of dyeing. He found that the action of acetylating and alkylating reagents upon cotton produces no change in its behavior towards certain named dyestuffs.

In further work upon the methylation of cellulose and the hydrolysis of the methylated derivatives so formed,[3] W. Denham and H. Woodhouse have determined that the formulae given in their previous work [4] are not to be taken as representing the composition of definite homogeneous methylcelluloses. Methylation being a progressive process without definite stages, the percentage of combined methoxyl increases with the number of successive treatments, products containing 23.89 and 25.975 methoxyl groups being obtained after six methylations.

1. E.P. 27491, 1911.
2. Monats. 1905, **26**, 413; abst. J.C.S. 1905, **88**, ii, 457.
3. J.C.S. 1914, **105**, 2357; abst. J.S.C.I. 1914, **33**, 1084.
4. See page 2508 of this work.

All the operations are accompanied by a loss in weight, particularly the sixth methylation, which was carried out with more concentrated sodium hydroxide (38.3 gms. per 100 cc.). The highly methylated preparations when hydrolyzed at 0° by means of hydrochloric acid saturated with the gas at that temperature,[1] undergo solution and hydrolysis without evidence of profound decomposition. These products of hydrolysis may be resolved by a complex series of fractionations with solvents (ether and acetone) and by the distillation of methylglucosides prepared from them, into a mixture of methylhexoses, no disaccharide being detected. The substances actually isolated may be classed into an amorphous dimethylglucose, crystalline trimethylglucose, and a trace of a crystalline compound, possibly a tetramethylglucose. No dextroses could be isolated, but strong presumptive evidence of the presence of unmethylated hexose was obtained.[2] It was proven that substantially the highest product of the methylation of cellulose is represented by trimethylglucose after hydrolysis, thus confirming the existence of three free hydroxyl groups in the original cellulose aggregate. The trimethylglucose isolated in the crystalline form amounted to 10% of the crude product. It did not yield an osazone.

Kinematograph Picture Films. In covering picture films with a resistant coating, F. Thompson [3] deposits the cellulose acetate or nitrocellulose in amyl acetate with a small quantity of castor oil, without closing the sprocket apertures.[4] The deposit when dry forms a film enclosing the gelatin film between it and the celluloid. In the formation of similar continuous films without the employment of silver sensitive salts, J. Thornton [5] forms the images of any desired color in pure dye or lake, the cellulose acetate or celluloid base being then

1. Willstaetter and Zechmeister, this work, page 2614.
2. The presence of small traces of tetramethylglucose may be due to the depolymerization of the cellulose during the methylation treatments or else to the existence of terminal dextrose residues in the cellulose molecule.
3. E.P. 20965, 1909. See also this work, Thompson, page 2871.
4. Compare E.P. 24556, 1909.
5. E.P. 4044, 1912. See also E.P. 26997, 1911; 3384, 12230, 14433, 1912. Compare J. Thornton, E.P. 5793, 1899; J.S.C.I. 1900, 19, 71, 157, 274, 559, 689; 1901, 20, 68; 1904, 23, 680.

coated with a bichromate sensitized colloid layer. The film is printed by exposing it for a lengthened time to a light of high actinic but low heating powder, and then treated in the usual manner.

The transparent material of F. Paschke [1] comprises coating one side of each of two glass sheets with a solution of cellulose acetate in tetrachlorethane, chloroform or other suitable solvent or solvent combination. The sheets are pressed together before the cellulose acetate films are quite dry. After drying, the sheet is treated with a suitable solvent by bringing the compound sheet together with small amounts of solvent aided by continued pressure. Sheets so formed have their outer surfaces the side next to the glass, and therefore are equally smooth and polished, being said to be admirably adapted for many uses where a flexible glass would be indicated.

In the manufacture of films from cellulose esters, H. Dreyfus [2] employs the mono- and di-glyceryl esters of the aromatic monocarboxylic acids, such as benzoic and naphthoic acids and their nuclear substitution products. Glycerol mono- and di-benzoates and naphthoates are said to be especially valuable cellulose acetate solvents and camphor substitutes.

According to A. Bacigalupi,[3] who has been granted a protection for the idea, an incombustible composition for printing-plates is composed of from 50-70% of cellulose acetate, from 20-40% of a mixture of tetrachlorethane and pentachlorethane, and from 5-10% of alcohol, benzol or other solvent.

Imitation engraved or chased metal plates are obtainable, according to the patented process of G. Moncany,[4] by embossing a material obtained by glueing together layers of metal foil and paper or paper pulp, and then coating the metallic side of this with a layer of gold, silver or copper powder. The embossed product may be painted in the hollow parts, and preferably coated with cellulose acetate.

Acetate Waterproofing Mixtures.. According to Tondl &

1. E.P. 15580, 1913; abst. C.A. 1915, 9, 137.
2. F.P. 461544, 1913; abst. C. A. 1914, 8, 3859.
3. E.P. 29273, 1910.
4. E.P. 14537, 1912.

Co.[1] collars, cuffs and shirt front covers composed of celluloid may be reinforced by the attachment of acetylcellulose sheets to decrease their inflammability. The collar may be advantageously strengthened by the insertion of a celluloid or cellulose acetate strip between the linen layer befor the latter is sewed up into the completed collar. In the rot-proofing of canvas for use in tire covers, W. Muntz[2] recommends impregnating the fabric with cellulose acetate or other cellulose esters in solutions of acetone, trichlorethylene, or the fabric may be directly treated with an acetylating or formylating bath to esterify the cellulose. The treated fabric may with advantage be combined with Egyptian cotton or with leather. R. Weeber[3] coats fabrics with alternate layers of a varnish composed of acetylcellulose or nitrocellulose by dusting each layer before applying the next succeding one with a powdered and preferably absorbent substance such as wood meal.

Acetate Cements and Adhesives. Artificial members of the body, such as legs, arms, hands, ears, noses or boots or extensions for short limbs, are composed of absorbent material such as lint coated or saturated with a non-inflammable celluloid such as cellulose acetate, the patentee, W. Longmate,[4] advises the application of successive layers of lint saturated with the cellulose ester for application to the cast of a limb as a stiffening material, the coat being further stiffened subsequently by coating with a heavy and viscous cellulose acetate lacquer.

J. Peck[5] prepares surgical splints, jackets and similar orthopedic appliances by covering the model of a limb or other part with gauze, afterwards coating or impregnating the gauze

1. E.P. 15782, 1913.
2. E.P. 613, 1912.
3. E.P. 951, 1910.
4. E.P. 3991, 1913. For cellulose acetate, see E. Lemaire, La Nature, 1908-9, 37, 130. The cellulose acetate cement composition of A. Tessler (U.S.P. 1122554, 1913) intended as a cement for continuous photographic films, is composed of 3% non-inflammable film material as cellulose acetate, 1% celluloid, 47% acetone, 21% chloroform and 21% glacial acetic acid, with or without aniline.
5. E.P. 23777, 1912. For the preparation of cellulose acetate in the presence of oxyacid esters or methylamine sulfate, see Knoll & Co., E.P. 2491, 4353, 16905, 1913. For the preparation of diethyl sulfate, see L. Lilienfeld, E.P. 13882, 1913. U.S.P. 1074633, 1913. D.R.P. 272339, 1913. F.P. 459282, 1913. Abst. C.A. 1913, 7, 4046; 1914, 8, 3100, 3340.

with a solution of celluloid rendered uninflammable by the addition of ammonium chloride or calcium chloride, or more preferably by substituting cellulose acetate in solution for the celluloid. The edges of the splint are bound with leather and the whole varnished with a solution of cellulose acetate or double ester of cellulose dissolved in acetone or other appropriate solvent.

H. Chalmers has described a waterproof cement especially applicable for joining leather belting, a satisfactory formula being to dissolve one pound of acetated cellulose in one-half gal. each of chlorofor mand acetone, subsequently adding one per cent. each phenol and castor oil.[3] The leather cement of H. Belnisch[4] is similar, larger proportions of oils and fatty bodies being added to the acetylcellulose to increase the pliability. Cellulose esters, combined with gelatin, form the basis of the synthetic india rubber of W. Plinatus.[5] The impregnating composition of L. Lilienfeld[6] comprises the combination of acetylcellulose, nitrocellulose or viscose with sulfur derivatives of alcohols and hydrocarbons, and is claimed as especially applicable for the waterproofing of textiles and the manufacture of waxed cloth, oilcloth, linoleum, transparent paper, lin-

3. U.S.P. 1112890, 1914; abst. C.A. 1914, 8, 3841. In Swiss P. 65057, being Add. to Swiss P. 63585, H. Dreyfus prepares a celluloid substitute by the treatment of acetylcellulose with insufficient amounts of non-reacting aromatic alcohols in conjunction with chlorine derivatives of acetylene, ethylene, methylene and ethylidine. Abst. K., 1914, 4, 370.

4. D.R.P. 279638, 1913; abst. K. 1914, 369. See Aust. P. 33508, same as E.P. 11164, 1902. Aust. P. 21614, same as D.R.P. 154657. See also Farb. v. Bayer & Co., Swiss P. 52903. Aust. Appl. 8776, 1910. Aust. P. 21213, 1905. A. Eichengruen, Swiss P. 51952. Knoll & Co., Aust. P. 33508, 34272, 1908; 41811, 1910; Be. P. 244950, 1912. Akt. f. Anilin Fabrikation, Be. P. 248907, 1912. Aust. P. 21213, same as F.P. 317007.

5. E.P. 25449, 25805, 1911; F.P. 450967; abst. Kunst. 1914, 4, 286. Compare E.P. 476, 1910.

6. E.P. 26928, 1910.

crusta, waterproof crpets, bed linings, tracing cloth and book binding cloth. The sulfur derivatives used are mercaptans, sulfides, polysulfides, mercaptals, sulfinic acid, sulfonic acid, sulfoxides and sulfones derived from propane, propylene, cyclopropane, thioglycerol, and the mono-, di, and tri-thiopyroglycides. As a specific example, the patentee cites the combination of paper treated with a thioglycerine or oxytrimethylenesulfide, which is heated until the transformation product has attained the desired consistency, when the cellulose ester is added, and the solvent evaporated, the residual product being the impregnating composition sought.

Explosives. C. van Pittius[7] has evolved a combination said to be suitable for explosives, in which an active substance such as liquid trinitrotoluene (a mixture of commercial di- and tri-nitrotoluene) is combined with nitrocellulose or the acetyl, propyl or nitro-acetyl celluloses. In a specific example cited, the patentee directs to combine 10 parts of dinitroacetinglycerin with 50 parts of liquid trinitrotoluene, in which the nitrated product completely dissolves. Thirty-eight parts of solid trinitrotoluene is then added, and 2 parts of a mixture of acetylcellulose and collodion cotton.

Phonograph Records. A. Eichengruen[8] has described a disc record consisting of any foundation, but usually shellac, which is coated with a thin film of a cellulose ester or cellulose acetate with solvent mixtures as alcohol and benzene, with or without the admixture of mineral constituents as gypsum or kieselguhr. This film is designed to protect the sound-grooves in the shellac foundation. The cellulose ester film is applied by dipping, spraying or by first forming thin sheets of paper, silk or foil and then laying one or more of these sheets upon the shellac mass and impressing in the usual manner. The film may also be prepared by drying the cellulose ester solution in thin plates or by cutting or peeling from thicker plates. The G. Koller composition for making films,

7. E.P. 25274, 1910; abst. C.A. 1912, **6**, 1527; J.S.C.I. 1911, **30**, 1281. E.P. 555, 26334, 1910.

8. E.P. 17574, 1912. Snowden & Co., Be. P. 241975, 1912, render cellulose acetate incombustible by means of aqueous boric acid.

varnishes and acetate silk is formed by treating acetylcellulose with phenol and trichlorethylene or perchlorethylene.[1]

J. and C. Bedford and J. Kirk[2] prepare a linoleum-like material for covering spinning rollers, consisting of a backing of cotton coated with a wood or cork dust composition protected by a cellulose acetate or pyroxylin varnish. For producing woven effects by printing, the Societe des Manufactures N. Konchine[3] dissolve cellulose and its derivatives in suitable solvents, which are then printed on the tissue by means of an engraved roller, a liquid precipitant for the cellulose being delivered on to the roller.

In the patented process for the manufacture of plastic substances from cellulose derivatives according to F. Lehmann,[4] cellulose esters are incorporated by the aid of solvents

1. U.S.P. 1079733, 1913; Be. P. 243162, 1912; abst. C.A. 1914, 8, 421. J. Bock (F.P. 469017; abst. Kunst. 1914, 4, 370) prepares water-insoluble, uninflammable pearls by combining cellulose acetate with "pearl essence." For a process for producing cellulose acetate soluble in ethyl acetate, see F. Collischon, F. Ruppert and Verein fuer Chemische Industrie in Mainz, U.S.P. 1109512, 1914; F.P. 455117, 1913; abst. J.S.C.I. 1913, 32, 865; 1914, 33, 958; C.A. 1914, 8, 3502. For cellulose alkyl esters prepared by treatment of cellulose with alkali, then with methyl sulfate or ethyl chloride, consult H. Dreyfus, F.P. 462274, 1912; abst. C.A. 1914, 3859. For modification of soubility of cellulose acetate, see E. Knoevenagel, Kunst. 1914, 4, 344.

2. E.P. 28293, 1909. See also E.P. 16102, 1902; 17430, 1903; 19066, 1904. For the Ramsey and Lewis method of manufacturing cellulose fatty acid esters, see E.P. 22718, 1914. See Belg. P. 261-288; abst. Kunst. 1914, 4, 393, same as F. P. 463498, 1913, page 2835. The W. Cohoe process of acetic acid manufacture is described in E.P. 23573, 1910, and the H. Sulzer method of formates manufacture is detailed in Belg. P. 242325, 1912. The Deutsche Gasgluelicht Aktges. (E.P. 75, 1915) describe methods for producing fatty acid esters of cellulose containing over 20% of combined fatty acid.

3. F.P. 469371, 1914; abst. J.S.C.I., 1915, 34, 26. The Chemische Werke vorm. H. Byk (Belg. P. 261693; abst. Kunst. 1914, 4 378) produce acetylcellulose lacquers by the employment of lactic acid esters as adjuncts and plastic-forming bodies, either in the presence or absence of hydrocarbons.

4. F.P. 469925, 1914; abst. J.S.C.I. 1915, 34, 25. The Soc. Chimique des Usines du Rhone, Anciennement Gilliard, P. Monnet et Cartier, F., E.P. 25893, 1911, produce cellulose acetates by treating cellulose with acetic acid and acetic anhydride vapors. The Verein feur Chemishe Industrie in Mainz, E.P. 19008, 1913, claim to have improved upon their E.P. 21628, 1901, for obtaining cellulose esters soluble in ethyl acetate, or for the production of an ester

with coumarone resin consisting of the resinous products formed by the polymerization of coumarone and indene in the refining of coal-tar oils. In an example of the process cited 200 gms. of coumarone resin are dissolved in a mixture of 100 grams each of ether, alcohol and benzene, and 700 gms. of nitrocellulose or acetylcellulose are incorporated with the solution in a manner similar to that employed in the manufacture of camphor containing plastic masses.

W. Beatty [1] in continuing his investigations upon the formation of plastic compounds containing dihydroxydiphenyldimethylmethane, has found that acetylcellulose may replace the nitrocellulose and the camphor substitutes described in E.P. 18822, of 1912.

of any other desired degree of solubility, by heating to a high temperature an aqueous solution of the ester in the absence of hydrolytically acting substances until the desired solubility is attained. In an example, an acetate prepared from cotton, glacial acetic acid and acetic anhydride and sulfuric acid, is treated with dilute acetic acid and sodium acetate and the mixture heated to 100-110° until a sample is found to be soluble in acetone. Products soluble in mixtures of acetone and in ethyl acetate may also be obtained.

1. E.P. 18499, 1913; abst. C.A. 1915, **9**, 377; see also E.P. 18822, 1912; C.A. 1914, **8**, 572. For a process for the formation of artificial silk, artificial threads or films from primary solutions of acetylcellulose see E. Dammann, D. R. Appl. D-29058, 1913; abst. Kunst. 1914, **4**, 396. For the formation of acetylcellulose solutions according to the process of the Badische Anilin u. Soda Fabrik, see D. R. Appl. St. 19374, 1914; abst. Kunst. 1914, **4**, 396, and the preparation of cellulose acetate lacquers, Societe Anonyme par Acations "La Solvea," compare D. R. Appl. S-42073, 1914; abst. Kunst. 1914, 4, 384. In a recent German patent application (V-11214, 1912; abst. Kunst. 1914, 4, 384) the Verein fuer chemische Industrie, Frankfurt, describe methods for the manufacture of non-fusible cellulose acetate masses and films, while L. Clement and C. Riviere (Bull Soc. d'Encouragement, 1914, **121**, 187; abst. J.S.C.I. 1915, **34**, 75) describe in detail the manufacture and application of cellulose acetate varnishes and coatings.

CHAPTER V.

ANALYSIS OF UNINFLAMMABLE CELLULOSE ESTERS.

The analytical determinations of the noninflammable esters of cellulose are but few in number, and comprise a determination of the organic acid radical, and the physical properties of solubility, viscosity and tensile strength when in films. The quantitative methods of cellulose analysis are given in Part One.

Estimation of Formic Acid. The acid may be titrated in dilute aqueous solution with sodium hydroxide solution, phenolphthalein being used as indicator. Each cc. normal sodium hydroxide is equivalent to 0.046 gms. absolute formic acid. The acid may also be estimated by the permanganate method of Jones,[1] as modified by J. Klein,[2] E. Rupp,[3] and H. Grossmann and A. Aufrecht.[4] The solution is made alkaline with sodium carbonate, an excess of N/10 permanganate added, and the mixture heated on the water bath for 30 minutes.[5] The solution is acidified and a known volume of standard oxalic acid run in, until the precipitate of manganese hydroxide has dissolved and the permanganate disappeared. The excess of oxalic acid is estimated by titration with permanganate. A volume of oxalic acid equal to that originally taken is also

1. Am. Chem. Jour. 1897, **17**, 539. For methods of obtaining formic acid in quantity see F. Chattaway, Chem. News. 1914, **109**, 109; abst. C.A. 1914, **8**, 2874. For hydrolysis of acetic acid, see J. Philip, Proc. C. S. 1913, **28**, 259; abst. C.A. 1913, **7**, 2931.

2. J. Klein, Ber. 1906, **39**, 2640; abst. J.S.C.I. 1906, **25**, 1010; J.C.S. 1906, **90**, ii, 812.

3. Zts. anal. Chem. 1906, **45**, 687; abst. J.S.C.I. 1906, **25**, 1070; J.C.S. 1906, **90**, ii, 907.

4. Ber. 1906, **39**, 2455; abst. J.S.C.I. 1906, **25**, 830; J.C.S. 1906, **90**, ii, 634.

5. The heating in the water bath is necessary, as at the ordinary temperature the oxidation requires from 6 to 10 hours for completion. In acid solution, the oxidation of formic acid by permanganate is not nearly completed after the lapse of ten hours. See A. Joseph, J.S.C.I. 1910, **29**, 1189; abst. C.A. 1911, **5**, 445; J.C.S. 1910, **98**, ii, 1118.

titrated with permanganate solution as a control, the quantity of permanganate used to oxidise the formic acid being determined by the difference between the result and the total permanganate used.

Or, a measured volume of the formic acid of not over 1% strength is placed in a stoppered flask, an excess of N/10 permanganate solution and 0.5 gms. of anhydrous sodium carbonate added, the whole being heated on the water bath 30-40 minutes. After cooling, 75 cc. water, 25 cc. dilute sulfuric acid and 2 gms. of potassium iodide are added, the liberated iodine being titrated with thiosulfate solution. Each cc. N/10 thiosulfate solution used is equivalent to 0.0023 grams of formic acid.

Other methods are the gravimetric reduction of mercuric chloride by formic acid,[6] by titrating mercuric chloride against potassium iodide.[7,8] In the H. Franzen and G. Greve method,[9] 7.5-15 gms. mercuric chloride dissolved in 100-200 cc. hot water, is added to a solution containing 0.2-1 gm. of formic acid per liter, as a soluble salt. The liquid is heated on the water bath and stirred until the precipitated mercurous chloride has settled. Sodium hydroxide is then added to the hot liquid until a brownish precipitate of mercuric oxide becomes permanent. The liquid is again heated on the water-bath, and, after the precipitate has completely settled, the neutralization is repeated. The precipitate is once more made to settle by heating on the water-bath, and then 20 cc. con-

6. H. Franzen and G. Greve, J. prakt. Chem. **80**, 368; abst. C.A. 1910, **4**, 886. See also Scala, J. Anal. and Appl. Chem., **5**, 233; Lieben, Monatsch. 1893, 746; Leys, Mon. Sci., **12**, 632. For the bromometric determination of formic acid, see H. Maeder, Apoth. ztg. 1912, **27**, 746; abst. J.S.C.I. 1912, **31**, 1006. For the preparation of alkali formates according to the method of W. Norris, consult E.P. 4684, 1910. For determination of nitrates with formic acid, see A. Quartaroli, Staz. sper. agrar. ital., **47**, 161; U. Molinari, Ib. **47**, 24; abst. C.A. 1914, **8**, 3766.

7. F. Auerbach and W. Pluddemann, Arb. Kais. Gesundheitsamt. **30**, 178; abst. C.A. 1910, **4**, 2080; J.C.S. 1909, **96**, ii, 355. Also, Portes and Ruyssen, Compt. rend. **82**, 1504.

8. H. Franzen and F. Egger, J. prakt. Chem. 1911, **83**, 323; abst. J.S.C.I. 1911, **30**, 572; C.A. 1911, **5**, 2477; J.C.S. 1911, 100, ii, 446. See also C.A. 1910, **4**, 886; J.S.C.I. 1909, **28**, 1222.

9. H. Franzen and G. Greve, J. prakt. Chem. 1909, **80**, 368; abst. J.S.C.I. 1909, **28**, 1222; C.A. 1910, **4**, 886.

centrated hydrochloric acid added, and the heating continued for one hour. The whole process of reduction requires about two and a half hours. The precipitate is collected in a Gooch crucible, well washed with hot water, dried in a steam oven for 6-8 hours, and then for several hours in a vacuum dessicator. The weight found multiplied by the factor 0.097726 gives the corresponding weight of formic acid.

Hydrochloric and oxalic acid in formic acid may be shown by the addition of silver nitrate. Acrolein and allyl alcohol are shown by neutralizing with sodium hydroxide, after which no acrid, pungent or acid smell should be noticeable.

Acetic Acid. Glacial acetic acid suitable for acetation should contain at least 99% absolute acid, and preferably 99.5%. If 9 volumes of oil of turpentine be agitated with one volume of acid, no cloudiness will be produced if the acid be 97% strength or upward. Acid of 99.5% strength is miscible with oil of turpentine in all proportions without turbidity.[1] A delicate test for the presence of water is to mix

1. Bardy, Chem. News, **40**, 78. For process for producing acetic acid from coal, lignite, etc., see J. Behrens, D.R.P. 275049, 1913; abst. J.S.C.I. 1914, **33**, 807. For the manufacture of highly concentrated acetic acid by the electrolytic oxidation of acetaldehyde and its polymers, see Konsortium f. Elektrochem. Ind. D.R.P. 274032, 1911; abst. C.A. 1914, **8**, 2984. For manufacture of actic acid from coffee husks, see G. Calvert, E.P. 10687, 1913; abst. C.A. 1914, **8**, 3489. For the E. French and J. Withrow process, consult U.S.P. 1104978, 1914. E. French and J. Withrow (U.S.P. 1104978, 1914; abst. J.S.C.I. 1914, **33**, 961) subject crude actic acid to hydrolysis in conjunction with a salt to remove pyroligneous substances and foreign volatile acids, the electrolysis being so regulated that no material decomposition of acetic acid takes place. The Farbwerke vorm. Meister, Lucius and Bruening (E.P. 10377, 1914; abst. J.S.C.I. 1914, **33**, 961) mix acetaldehyde with about 1% of its weight of a catalyst, especially ceric ovide, which is treated with oxygen under a pressure of about 2 atrospheres, or with air at a somewhat higher pressure, for 5 hours, cooling being resorted to after the temperature rises spontaneously to 50-60°; 95% of the theoretical amount of glacial acetic acid is thereby produced. According to the Naamlooze Vennootschap Fabrik van Chem. Produkten (E.P. 12042, 12130, 1913; abst. C.A. 1914, **8**, 3618, 3619) anhydrides of monobasic carboxylic acids are prepared by heating alkali or alkaline earth salts of acylsulfuric acids either alone, or in the presence of a salt of a carboxylic acid and free organic acid. By this process simple or mixed anhydrides are obtainable. Sodium acetylsulfate and sodium propionate, e. g., give rise to acetic-propionic anhydride. In the J. Behrens process (D.R.P. 275049, 1913; abst. C.A. 1914, **8**, 3359) acetic acid may be manufactured from hard coal or brown coal, the ethylene isolated

the acid with an equal bulk of carbon bisulfide and warm slightly; in presence of a trace of water the liquid becomes turbid.

Undoubtedly the most rapid and accurate method of determination of small amounts of water in glacial acetic acid acid is by observation of the congealing point. It is merely necessary to cool the container of glacial acetic acid and contents to about 14° or lower, rub a thermometer on the bottom or sides of the container until crystals commence to form, then stir until the temperature rises to the crystallizing point. The entire operation requires but a few minutes time and may be indefinitely repeated without loss of acid. From the congealing temperature found, the percentage of acetic acid is read off from the following table:

TABLE I.

CONGEALING POINTS OF CONCENTRATED ACETIC ACID.

Percentage of Acetic Acid	Congealing Point	Percentage of Acetic Acid	Congealing Point	Percentage of Acetic Acid	Congealing Point
100.00	16.63°	99.45	15.57°	98.8	14.32°
99.95	16.53	99.40	15.48	98.70	14.13
99.90	16.43	99.35	15.38	98.60	13.94
99.85	16.34	99.30	15.29	98.55	13.75
99.80	16.24	99.25	15.19	98.40	13.56
99.75	16.15	99.20	15.10	98.3	13.37
99.70	16.05	99.15	15.00	98.2	13.17
99.65	15.96	99.10	14.91	98.10	12.98
99.60	15.86	99.05	14.81	98.0	12.79
99.55	15.77	99.00	14.71	....	....
99.50	15.67	98.9	14.52	....	....

Acetic anhydride is readily distinguished from acetic acid by the miscibility of the latter with water, and its ready

from coal distillation being converted—by mixing with carbon dioxide and heating the mixture to about 400°—into aldehyed as an intermediate product, which is then further oxidized or reduced. R. Muller and the Deutsche Celluloid Fabrik (F.P. 468963, 1914; abst. J.S.C.I. 1914, 33, 916) prepare acetic anhydride is almost theoretical yield by passing the vapors of nitric anhydride or a mixture of nitrogen oxides with air or oxygen over calcium or sodium acetates. If the materials used are not dried, mixtures of acetic acid and anhydride are formed. The anhydride or mixture of anhydride and acid may be separated from the nitrate by vacuum heat or by extraction. The product is said to contain only traces of nitrogen and these may be separated by distillation over acetates. This process is applicable to the production of propionic or butyric tnhydrides.

congelation. F. Klein [2] boils a specimen with a small crystal of selenious oxide, or preferably sodium selenite. The anhydride gives a red precipitate of amorphous selenium, while with glacial acetic acid an absolutely clear solution is produced. A method of detecting and estimating small amounts of acetic anhydride in acetic acid has been developed by M. Edwards and K. Orton [3] and is based on the fact that certain aniline derivatives, notably 2-4-dichloraniline, react with acetic anhydride with great rapidity. The anilide can be accurately separated from the aniline derivatives, and then indirectly estimated in the form of chloroamine. The acetic anhydride is treated with the dichloraniline, extracted with methylene chloride after standing for a few hours at 16°, then separated by shaking with 10% HCl.

Several methods for the determination of formic in acetic acids have been proposed, as those of H. Delahaye,[4] P. Pikos,[5]

2. J. Ind. Eng. Chem. 1910, **2**, 389; abst. J.S.C.I. 1910, **29**, 1200; J.C.S. 1911, **100**, ii, 340.

3. Proc. Chem. Soc. 1911, **27**, 120, 121; J.C.S. 1911, **99**, 1181; abst. J.S.C.I. 1911, **30**, 681; C.A. 1911, **5**, 3561.

4. Ann. Falsif. 1910, **3**, 386; abst. J.S.C.I. 1910, **29**, 1200; C.A. 1911, **5**, 737. For the W. Beatty process of acetic anhydride manufacture refer to U.S.P. 1113927, 1914; abst. C.A. 1914, **8**, 3840. For rate of hydration of acetic, propionic, butyric and benzoic anhydrides, see B. Wilsdon and N. Sidgwick, J.C.S., 1914, **103**, 1959; abst. C.A., 1914, **8**, 906. For manufacture of acetic anhydride with sulfuryl chloride, refer to E.P. 23923, 1910. For acetic and propionic anhydrides, see F. de Jahn, E.P. 5939, 1910. J. Ekeley and C. Slater (J.A.C.S., 1914, **36**, 603; abst. C.A., 1914, **8**, 3792) have described the action of acetic anhydride upon benzylideneanthranilic acids.

5. Chem. Ztg. **32**, 906; abst. Chem. Zentr. 1908, **79**, II, 1501; C.A. 1909, **3**, 2281. For the detection and estimation of mineral acids in acetic acid, see P. Schidrowitz, Anal. 1903, **28**, 233; abst. J.C.S. 1903, **84**, ii, 700. For processes of acetic acid manufacture see Hoesch & Co. and M. Platsch, E.P. 5810, 1913. Konsortium f. Elektrochemische Industrie, E.P. 16849, 19016-7-8, 1913. G. Meunier, E.P. 12207, 1911; abst. C.A. 1912, **6**, 3518; J.S.C.I., 1912, **31**, 656. R. Swinton, E.P. 4976, 1910. A. Deiss and C. Fournier, E.P. 19679, 1910. E. Pohl, E.P. 25570, 1911; abst. J.S.C.I. 1912, **31**, 1196. O. Soederlund, E.P. 28609, 1911; abst C.A., 1913, **7**, 958; J.S.C.I., 1913, **32**, 524. G. Guignard, E.P. 3261, 1913. F. von Walther, E.P. 304, 1912. For the distribution of acetic and succinic acids between water and solutions containing two organic liquids, see W. Eastlake, Trans. Roy. Soc. Can. Sect. iii, **7**, 210; abst. C.A. 1914, **8**, 3741.

H. Fincke,[6] Freyer,[7] and H. Ost and F. Klein.[8] In the latter method the acetic acid is neutralized with alkali and titrated with permanganate. Other substances which reduce permanganate must be absent.

Acetic Anhydride may, like acetic acid, be conveniently determined by titration with standard alkali after hydrolysis into acetic acid, recalling that one molecule or 102 parts of acetic anhydride combines with one molecule or 18 parts of water to form two molecules or 120 parts of aceti cacid. Therefore, in acidity, 120 grams of acetic anhydride after hydrolysis is equivalent to 120 grams of acetic acid, or 100 grams of acetic anhydride to 117.65 grams of absolute acetic acid. One cc. normal alkali is equivalent to 0.05088 grams of acetic anhydride. The acetic anhydride to be examined is weighed off and shaken with about fifty times its volume of carbon dioxide-free distilled water, until oily drops disappear and a homogeneous solution results, or the mixture may be weighed out in a small glass bulb and then broken after immersion into a known quantity of standard barium hydroxide solution. When sodium or potassium hydroxide is used as the neutralizant, the excess of alkali is immediately titrated back with standard acid, phenolphthalein or azolitmin being used as indicator. If barium hydroxide is employed, the flask containing the anhydride and baryta solution is fitted to a reflux condenser and the contents warmed until the anhydride has all changed into acetic acid.

With either alkali, the excess of alkali titrated back with standard acid is deducted from the otal alkali required, the balance being the alkali consumed in neutralizing the acetic acid. Having found the percentage of acetic acid in the sample under examination, reference to the following tables gives without calculation the equivalent percentages of both acetic acid and acetic anhydride in the sample of acetic anhydride

6. Apoth. Ztg. 1910, 727. Pharm. J. 1911, 9; abst. J.S.C.I. 1911, 80, 82; Drug Circ. 1910, 54, 569.

7. Chem. Ztg. 1895, 1184. See also C. Rossi, L'Industria Chimica 1904, 6, 253; Chem. Centr. 1904, 75, II, 1165; J.S.C.I. 1904, 23, 1113.

8. Chem. Zts. 1908, 32, 815; abst. J.C.S. 1908, 94, ii, 903.

TABLE II.

ACIDITY OF MIXTURES OF ACETIC ACID AND ACETIC ANHYDRIDE.

Total Acidity by Titration.	Equivalent to a Mixture of		Total Acidity by Titration.	Equivalent to a Mixture of	
	Acetic Anhydride.	Acetic Acid.		Acetic Anhydride.	Acetic Acid.
100. %	—	100%	109.00	51	49
.2	1%	99	.19	52	48
.38	2	98	.37	53	47
.53	3	97	.52	54	46
.72	4	96	.70	55	45
.90	5	95	.88	56	44
101.08	6	94	.24	58	42
.26	7	93	110.08	57	43
.42	8	92	.40	59	41
.60	9	91	.58	60	40
.76	10	90	.77	61	39
.95	11	89	.95	62	38
102.12	12	88	111.12	63	37
.32	13	87	.28	64	36
.50	14	86	.45	65	35
.68	15	85	.62	66	34
.86	16	84	.80	67	33
103.02	17	83	.98	68	32
.20	18	82	112.14	69	31
.38	19	81	.32	70	30
.52	20	80	.45	71	29
.72	21	79	.60	72	28
.88	22	78	.80	73	27
104.08	23	77	113.00	74	26
.26	24	76	.23	75	25
.41	25	75	.38	76	24
.60	26	74	.55	77	23
.78	27	73	.73	78	22
.95	28	72	.90	79	21
105.13	29	71	114.10	80	20
.30	30	70	.28	81	19
.48	31	69	.47	82	18
.67	32	68	.61	83	17
.83	33	67	.80	84	16
106.00	34	66	.98	85	15
.20	35	65	115.17	86	14
.38	36	64	.35	87	13
.53	37	63	.52	88	12
.72	38	62	.71	89	11
.90	39	61	.90	90	10
107.08	40	60	116.10	91	9
.24	41	59	.27	92	8
.40	42	58	.46	93	7
.58	43	57	.65	94	6
.78	44	56	.82	95	5
.95	45	55	117.02	96	4
108.12	46	54	.20	97	3
.28	47	53	.36	98	2
.48	48	52	.50	99	1
.66	49	51	117.65	100	0
.82	50	50			

under examination, it being assumed that the only impurity likely to be present in the acetic anhydride is acetic acid (i. e. water).[1]

For instance, the first expression means that an acidity of 117.65% indicates the mixture consists of $100% of acetic anhydride and no percentage of absolute acetic acid, and hence no water. The last expression indicates that an acidity of 100% shows the presence of 100% of acetic acid and hence no percent of acetic anhydride. See also, the expression (say) total acidity of 108.82% shows the mixture to be composed of 50% by weight of acetic anhydride and 50% by weight of absolute acetic acid.

As will be observed from Table II., the estimation of acetic anhydride by titration is not a very exact determination, approximately two-tenths of one per cent. in total acidity causing a variation of one per cent. in acetic anhydride content. Titration therefore should be supplemented by gravity determination or refractometer reading as a check.

Sometimes it is desirable to calculate the strength of a commercial acetic anhydride upon the assumption that the acidity is unchanged anhydride and the balance water, i. e., that hydrolysis into acetic acid has not occurred and the composition of the anhydride under examination is composed of acetic anhydride and water, the same as commercial acetic acid comprises acetic acid and water only. In such cases the titration is conducted as above stated, reference being made to the following table, where the total acidity is calculated into the equivalent of acetic anhydride and of water.

1. Example: 80 per cent (grams) acetic acid plus 20 grams of acetic anhydride, gives 100 per cent of a mixture, which mixture titrates 103.52 per cent by weight of absolute acetic acid. It will therefore be seen that any mixture of acetic acid and acetic anhydride may be determined by a single titration and reference to above table. In an esterizing solution comprising acetic acid, acetic anhydride and sulfuric or other mineral acid, titration as above, with subtraction for the mineral acid found by volumetric titration (hydrochloric acid) or by precipitation (sulfuric acid) gives the percentage of both acetic acid and acetic anhydride. For the manufature of anhydrides of monobasic carboxylic acids, see Naamlooze Vennootschap Fabrik van Chemische Produkten, E.P. 12042, 1913. F.P. 461540, 1913; abst. J.S.C.I. 1914, 33, 219, 807.

TABLE III.

CALCULATION OF ACETIC ACID ANHYDRIDE BY TITRATION.

Total Acidity as of Acetic Acid.	Equivalent to a Mixture of		Total Acidity as of Acetic Acid.	Equivalent to a Mixture of	
	Acetic Anhydride.	Water.		Acetic Anhydride.	Water.
100.0	85.	15.	.8	.48	.52
.2	.17	14.83	109.0	.65	.35
.4	.34	.66	.2	.82	.18
.6	.51	49	.4	93.16	6.84
.8	.68	.32	.8	.33	.67
101.0	.85	.15	110.	93.50	6.50
.2	86.02	13.98	.2	.67	.33
.4	.19	.81	.4	.84	.16
.6	.36	.64	.6	94.01	5.99
.8	.53	.47	.8	.18	.82
102.0	.70	.30	111.0	.35	.65
.2	.87	.13	.2	.52	.48
.4	87.04	12.96	.4	.69	.31
.6	.21	.79	.6	.86	.14
.8	.38	.62	.8	95.03	4.97
103.0	.55	.50	112.0	.20	.80
.2	.72	.28	.2	.37	.63
.4	.89	.11	.4	.54	.46
.6	88.06	11.94	.6	.71	.29
.8	.23	.77	.8	.88	.12
104.0	.40	.60	113.0	96.05	3.95
.2	.57	.43	.2	.22	.78
.4	.74	.26	.4	.39	.61
.6	.91	.09	.6	.56	.44
.8	89.08	10.92	.8	.73	.27
105.0	.25	.75	114.0	.90	.10
.2	.42	.58	.2	97.07	2.93
.4	.59	.41	.4	.24	.76
.6	.76	.24	.6	.41	.59
.8	.93	.07	.8	.58	.42
106.0	90.10	9.90	115.0	.75	25
.2	.27	.73	.2	.92	.08
.4	.44	.56	.4	98.09	1.91
.6	.61	.39	.6	.26	.74
.8	.78	.22	.8	.43	.57
107.0	.95	.05	116.0	.60	.40
.2	91.12	8.88	.2	.77	.23
.4	.29	.71	.4	.94	.06
.6	.46	.54	.6	99.11	.89
.8	.63	.37	.8	.28	.72
108.0	.80	.20	117.0	.45	.55
.2	.97	.03	.2	.62	.38
.4	92.14	7.86	.4	.78	.22
6.	.31	.69	.65	100.	.00

A good commercial acetic anhydride will titrate equivalent to 85-90% acetic anhydride, and will give no, or at most but a faint reaction of hydrochloric acid with nitric acid and silver nitrate.

Index of Refraction. The index of refraction is an excellent instrument for the determination of mixtures of acetic acid and acetic anhydride (comemrcial acetic acid anhydride) and is based upon the observations of Landolt,[1] who found the molecular refraction of acetic acid to be 1.380.17 and that of acetic anhydride under the same conditions to be 1.39927, a variation of 191 in the fourth decimal. The refractometer also possesses the advantage of allowing determinations to be made upon small quantities. Any standard instrument is suitable, the deviation being read off, compared with the results in Table IV., which gives percentages of both acetic acid and anhydride by simple inspection.

Density. Acetic acid absolute has a density of 1.0495 at 20/4°, and acetic anhydride a density of 1.0816 at 20/4°, a variation of 321 in the fourth decimal. That is, the difference of one percent of acetic acid in commercial acetic anhydride will affect the density by about 0.00321 at 20°. Density of commercial acetic acid anhydride is readily taken by means of a 50 cc. picnometer carrying thermometer, the weighing in grams being multiplied by two to obtain the gravity, and this compared directly with Table V. gives the percentage composition by weight of both acetic acid and anhydride in the commercial acetic anhydride. For example, supposing the contents of the picnometer weighed 53.915 gm. Multiply by two gives 107.83 and inspection of Table V. shows this to correspond in gravity with a commercial anhydride composed of 90% acetic anhydride and 10% absolute acetic acid (both by weight).

1. Landolt, Pogg. Ann. 1862, 117, 353.

TABLE IV.

REFRACTOMETRIC DETERMINATION OF ACETIC ANHYDRIDE.

Refraction	Equivalent to Acetic Anhydride.	Equivalent to Acetic Acid.	Refraction	Equivalent to Acetic Anhydride.	Equivalent to Acetic Acid.
1.38017	0%	100%	1.389720	50%	50%
1.38036	1	99	1.389911	51	49
1.38055	2	98	1.390102	52	48
1.38074	3	97	1.390293	53	47
1.380934	4	96	1.390484	54	46
1.381125	5	95	1.390765	55	45
1.38132	6	94	1.390866	56	44
1.38151	7	93	1.391057	57	43
1.38170	8	92	1.391248	58	42
1.38189	9	91	1.391439	59	41
1.38208	10	90	1.391630	60	40
1.382271	11	89	1.391821	61	39
1.382462	12	88	1.392012	62	38
1.382653	13	87	1.392203	63	37
1.382444	14	86	1.392394	64	36
1.383035	15	85	1.392585	65	35
1.383226	16	84	1.392776	66	34
1.383417	17	83	1.392967	67	33
1.383608	18	82	1.393158	68	32
1.383799	19	81	1.393349	69	31
1.383990	20	80	1.393540	70	30
1.384181	21	79	1.393731	71	29
1.384372	22	78	1.393922	72	28
1.384563	23	77	1.394113	73	27
1.384754	24	76	1.394304	74	26
1.384945	25	75	1.394495	75	25
1.385136	26	74	1.394686	76	24
1.385327	27	73	1.394877	77	23
1.385518	28	72	1.395068	78	22
1.385709	29	71	1.395259	79	21
1.385900	30	70	1.395450	80	20
1.386091	31	69	1.395641	81	19
1.386282	32	68	1.395832	82	18
1.386473	33	67	1.396023	83	17
1.386664	34	66	1.396214	84	16
1.386855	35	65	1.396405	85	15
1.387046	36	64	1.396596	86	14
1.387237	37	63	1.396787	87	13
1.387428	38	62	1.396978	88	12
1.387619	39	61	1.397168	89	11
1.387810	40	60	1.397360	80	10
1.388001	41	59	1.397551	91	9
1.388192	42	58	1.397742	92	8
1.388383	43	57	1.397933	93	7
1.388574	44	56	1.398124	94	6
1.388765	45	55	1.398315	95	5
1.388956	46	54	1.398506	96	4
1.389147	47	53	1.398697	97	3
1.389338	48	52	1.398888	98	2
1.389529	49	51	1.399079	99	1
			1.399270	100	0

TABLE V.

ESTIMATION OF MIXED ACETIC ACID AND ACETIC ACID ANHYDRIDE BY MEANS OF DENSITY DETERMINATION.

Density 20°/4°	Equivalent to a Mixture of		Density 20°/4°	Equivalent to a Mixture of	
	Acetic Anhydride.	Acetic Acid.		Acetic Anhydride.	Acetic Acid.
1.0495	0%	100%	1.065550	50	50
1.049821	1	99	1.065871	51	49
1.050142	2	98	1.066192	52	48
1.050463	3	97	1.066513	53	47
1.050784	4	96	1.066834	54	46
1.051105	5	95	1.067155	55	45
1.051426	6	94	1.067476	56	44
1.051747	7	93	1.067797	57	43
1.052068	8	92	1.068118	58	42
1.052389	9	91	1.068439	59	41
1.052710	10	90	1.068760	60	40
1.053031	11	89	1.069081	61	39
1.053352	12	88	1.069402	62	38
1.053673	13	87	1.069723	63	37
1.053994	14	86	1.070044	64	36
1.054315	15	85	1.070365	65	35
1.054636	16	84	1.070686	66	34
1.054957	17	83	1.071007	67	33
1.055278	18	82	1.071328	68	32
1.055599	19	81	1.071649	69	31
1.055920	20	80	1.071970	70	30
1.056241	21	71	1.072291	71	29
1.056562	22	78	1.072612	72	28
1.056883	23	77	1.072933	73	27
1.057204	24	76	1.073254	74	26
1.057525	25	75	1.073575	75	25
1.057846	26	74	1.073896	76	24
1.058167	27	73	1.074217	77	23
1.058488	28	72	1.074538	78	22
1.058809	29	71	1.074859	79	21
1.059130	30	70	1.075180	80	20
1.059541	31	69	1.075501	81	19
1.059772	32	68	1.075822	82	18
1.060093	33	67	1.076143	83	17
1.060414	34	66	1.076464	84	16
1.060735	35	65	1.076785	85	15
1.061056	36	64	1.077106	86	14
1.061377	37	63	1.077427	87	13
1.061698	38	62	1.077748	88	12
1.062019	39	61	1.078069	89	11
1.062340	40	60	1.078390	90	10
1.062611	41	59	1.078711	91	9
1.062982	42	58	1.079032	92	8
1.063303	43	57	1.079353	93	7
1.063624	44	56	1.079674	94	6
1.063945	45	55	1.079995	95	5
1.064266	46	54	1.080316	96	4
1.064587	47	53	1.080637	97	3
1.064908	48	52	1.080958	98	2
1.065229	49	51	1.081279	99	1
			1.081600	100	0

Method of Menschutkin and Wasiljeff. This is based upon the reaction between acetic anhydride and freshly distilled aniline, which unite molecule for molecule with the formation of acetanilide with the liberation of one molecule of acetic acid. Acetic acid itself is said not to form acetanilide under these conditions. Two to four grams of the acetic anhydride to be examined are shaken with from 4 to 8 grams of freshly fractionated aniline, in a dry weighing bottle. The anhydride immediately combines with the aniline with the liberation of considerable heat. Upon cooling the contents of the weighing bottle, which has meanwhile become semi-solid, is washed into an ordinary beaker by means of absolute alcohol, phenolphthalein added, and the total amount of acetic anhydride present titrated with half-normal alkali.

While it is true that concordant results are usually obtained, yet the results are prone to be too high, due to the fact that although acetic acid does not react upon aniline in the cold, it does readily react at the temperature of union between aniline and acetic anhydride. On the other hand, if the temperature is kept down when the acetic anhydride is added to the aniline, maximum formation of acetanilid does not take place, and results obtained do not duplicate, too high values being obtained in the titration, and hence unduly high values are obtained for the amount of acetic anhydride present.

Analysis of the Cellulose Acetates. Moisture. Two to ten grams of the sample, previously comminuted to a fine powder, is placed in a tared watch glass, and dried at a temperature of 90-100° until no further loss in weight occurs. The moisture will be from two to six per cent.

Ash. Five grams are ignited in a platinum crucible over a Bunsen burner, or preferably in a muffle oven. A small quantity of ammonium carbonate is then added and the mass fused until constant weight is obtained. The ash will seldom exceed 1.5%, and will usually vary between 0.4-0.6%.

Solubility. From three to five grams of the fine powder is shaken in a flask with 100 cc. of the solvent combination in which it is proposed to use the cellulose ester under examination, solution being facilitated by means of shot or small

porcelain balls, agitation being continued until all has passed into solution. A mixture of three volumes of tetrachlorethane and one volume of 95% ethyl alcohol is an excellent combination to determine the relative solubility of cellulose esters, as is also acetone of 99% strength or purer. After solution has been completed the amount of insoluble matter may be determined by filtration of an aliquot portion through a counterpoised filter paper, finally washing the filter with solvent of the composition first used, until the filtrate gives no solids upon drying. The filter paper is dried and reweighed.

Viscosity. Determination of viscosity is of considerable importance in the working up of the organic esters of cellulose, especially in the manufacture of lacquers, filaments and films, because it admits of an estimation of the suitability of the various esters for specific purposes. For dilute solutions, containing from 3-5 grm. per 100 cc. an ordinary Redwood or similar viscosimeter is suitable, the number of minutes required for a stated volume to pass through the orifice at a temperature of 17.5° or 25° being compared directly either with water, rape seed oil, or the fluid portion of the cellulose ester solution tested. By working under identical conditions, comparable results are readily obtained. For heavier solutions, a Cochius or Henry viscosimeter is preferable, as detailed in Volume One. The principle of the Cochius viscosimeter is the measurement of the time required for a bubble of air of a predetermined size to pass through a solution of the cellulose ester in a known solvent mixture at a stated temperature and definite strength of ester.

The Henry viscosimeter depends upon the time required for a steel or porcelain ball or a float to pass through a long tube filled with the ester solution of known strength and temperature, the density of the ball used depending upon the concentration of the cellulose ester solution, and the viscosity of which it is desired to determine. The proportion of the time

1. See G. Noyer, "Viscosity of Cellulose Acetates," Caout. et Guttap. 1913, **10**, 6875, 7009; abst. C.A. 1913, **7**, 2303; Kunst. 1913, **3**, 352.

found to that required is ascertained by the passage of the same ball through the fluid portion of the solution or by comparing with a standard acetated cellulose solution of same total solid content. To obviate inaccuracies caused by air bubbles, it is often of advantage to place the solution the viscosity of which it is desired to determine under an air pump and exhaust the air dissolved therein. Either pure acetone or a mixture of 60 parts tetrachlorethane and 40 parts 95% ethyl alcohol (both by volume) is a satisfactory standard liquid for purposes of comparison. The identical temperature of the solution to be determined and the control used as a standard is assured by allowing the two solutions to remain together for several hours before the determination is made.

Tensile Strength. A portion of the solution used for viscosity determinations above is poured on a flat, scrupulously clean glass or nickel plated surface, and allowed to evaporate to dryness away from draughts of air. Placing a fine mesh sieve over the drying film will usually intercept air currents and admit of a film of smooth surface being formed. The general appearance of the film when examined with a low power magnifying glass, freedom from unacted-upon fibers and extraneous impurities and transparency and color are the points usually looked for. The film, after assurance that all solvent has been removed, is tested by means of a dynamometer as explained in Volume Five, and the elongation per square millimeter ascertained. The permeability of the film to water may be determined by measuremnt of the diameter of the film before and after prolonged soaking in water, but porosity determinations are seldom resorted to. They are of value in continuous photographic films, where the alignment of the sprocket holes in the film is most important.

Stability Tests. The cellulose acetates possess the defects of instability similar to the corresponding nitric esters, but as the results of cellulose acetate instability are not made known in a disasterous manner, the question of instability in uninflammable cellulose esters has not been given as much thought and attention as with the nitrocelluloses.

An approximate idea of instability may be gained by weighing 5-10 grm. of finely powdered cellulose acetate on a watch glass or shallow weighing flask, which contains two pieces of azolitmin paper, one blue and the other neutral. The cover of the flask is loosely attached, or with a watch glass it is covered with another of the same size, and the whole placed in a drying oven which is kept at a temperature of 95-100°. With acetylcellulose of satisfactory stability, the neutral color should remain without change for at least 24 hours, and the blue paper ought to acquire a neutral tinge before 48 hours.

A more satisfactory test is to introduce 5 grm. of finely divided acetylcellulose into an Emmerling drying apparatus, or into a U-tube of 15-20 mm. diameter and 175 mm. height. The whole is completely immersed in an oil-bath which is kept at a temperature of within two degrees of 125°. A very slow current of carbon dioxide-free air is aspirated through, the acetic acid generated being carried away and absorbed in a receiver containing 1/20 or 1/50 normal sodium hydroxide. After three hours' aspiration, a titration of an aliquot portion of the caustic soda solution is made, the acidity present conveying a fair idea of the stability of the cellulose acetate under examination. The "stability factor" should not exceed 5 in a carefully prepared ester, the "stability factor" being the amount of acetic acid in grams liberated under the above conditions from 100 grm. of material.

Determination of the Copper Number. The determination of the "Copper Number" is of interest because it is closely related to the quality of cellulose acetate. The smaller it is, the greater is the tenacity and viscosity of the cellulose ester solution. A maximum limit of 10% may be considered a value which should never be substantially higher. Two grms. of finely divided material are digested with 30 cc. water for 30 minutes at 60-70° in an Erlenmeyr flask, the mass being shaken several times to keep the material thoroughly disintegrated. Next 100 cc. Fehling's or Pasteur's solution is added, and the whole allowed to remain on the water-bath for one hour. The flask is then connected with a reflux condenser in order to prevent concentration of the liquid from evaporation, and

boiled vigorously. After standing ten minutes the solution is filtered, and the precipitate washed with boiling distilled water until neutral. The copper on the filter paper is then assayed either by ignition or electrolysis. For full discussion of the import of the "copper number," consult Volume One.

Determination of Acid Radicals.[1] The quantitative determination of acetic acid and homologous radicals in cellulose acetate and similar esters may be accomplished by one of the four following methods:

(a) *Method of A. Green and A. Perkin.*[2] About 0.4 grm. is allowed to swell up in 30 cc. ethyl alcohol (substantially absolute), and 2 cc. concentrated sulfuric acid. The whole is then carefully and slowly distilled. When the liquid in the distillation flask has decreased to about half its volume, fresh alcohol is added, and this repeated three times, the distillation being continuous. The acetated cellulose gradually passes into solution, a clear liquid being finally obtained, containing at most only negligible traces of undissolved material. The ethyl acetate thus formed by the esterification of the ethyl alcohol and the acetic acid from the acetylcellulose is condensed and allowed to run into standard alkali solution in

1. For proposed method of determination of the molecular weights of cellulose acetates by the freezing point method, see Chem. News 1892, **66**, 40.

See W. Beck, dissertation, Leipzig, 1913; C.A. 1913, **7**, 1608, for the determination of acetic acid in acetylcelluloses.

For the determination of acetyl groups in organic compounds see F. Wenzel, Monats, 1897, **18**, 659; abst. J.C.S. 1898, **74**, i, 234. For simple method of determining acetyl groups, consult J. Sudborough and W. Thomas, Proc. C.S. 1905, **21**, 88; abst. J.S.C.I. 1905, **24**, 652. In their process, from one-half to one grm. of the acetyl derivative is treated with a 10 per cent. solution of pure benzene sulfonic acid (or naphthalene- *a*-, or *b*-sulfonic acid), and the mixture distilled with steam until the distillate is no longer acid. The distillate is then titrated with a standardised solution of barium hydroxide, using phenolphthalein as indicator. With O-acetyl compounds the distillation takes from one to two hours, but somewhat longer with N-acetyl derivatives. The pure benzenesulfonic acid used can be prepared by blowing steam through a solution of the barium salt until the distillate is neutral, then allowing the solution to crystallise, and decomposing the purified barium salt with the theoretical quantity of sulfuric acid.

2. J.C.S., 1906, **89**, 811; abst. Chem. Centr. 1906, II, 221; J.S.C.I. 1906, **25**, 652; Jahr. Chem., 1905-08, II, 985; Zts. ang. Chem., 1907, **20**, 459. See also J.C.S., 1904, **85**, 1462; **87**, 107; 1907, **91**, 1230.

excess, the alkali being titrated back to neutrality at the close of the distillation process. When the fractionation is properly conducted, the distillate is almost colorless, but if the latter be allowed to proceed too far, darkening of the solution occurs, accompanied by a reduction of the sulfuric to sulfurous acid, and the analysis is vitiated from the presence of sulfurous acid in the distillate. In applying this method unrestricted to a large variety of esters, in various combinations, the conditions favorable to the formation of ethyl acetate and analogous compounds must be taken into consideration. A complete saponification of the acetylcellulose is indicated by the fact that at the end of the operation a clear solution is obtained.

(b) *Method of H. Ost.*[1] Two or three grams of cellulose acetate, carefully dried and preferably finely comminuted, is dissolved in a cold mixture of equal volumes concentrated sulfuric acid and carbon dioxide-free distilled water, and allowed to stand at room temperature for two days for the cellulose ester to pass into solution. It is then diluted with water and distilled with a current of steam, continuing for four or five hours, and receiving the distillate in N/10 NaOH or KOH, or more preferably standard barium hydroxide solution.[2] The distillate is made up to a known volume, and aliquot portions titrated back to neutrality with standard acid. The method is accurate and reliable when certain precautions are carefully observed. All the water used should be free from carbon dioxide. The distillate should give no opalescence with barium chloride. The amount of fluid in the distilling flask should be maintained constant. Distillation of four hours gives the best results. For most satisfactory results it is necessary to titrate, then allow more distillate to form and titrate again, to determine definitely when all the acetic acid has been vaporized. This interruption several times of the

1. Zts. ang. Chem. 1906, **20**, 995; abst. J.S.C.I. 1906, **25**, 606.

2. The value of receiving the distillate in standard baryta solution is that any traces of carbonates or carbon dioxide will be immediately noticeable by a turbidity due to the precipitation of barium carbonate. In this connection see "Analysis of Cellulose Esters," V. Hottenroth, Chem. Ztg. 1914, **38**, 515; abst. C.A. 1914, **8**, 2944; Kunst. 1914, **4**, 239.

distillation does not tend to increase the accuracy of the determination. The limits of error of this process are given as 1.5-2%.

From the percentage of acetic acid found, calculation into cellulose acetate is made in the usual manner.

Sodium Ethylate Method of Cross and Bevan. Saponification is carried out by allowing the ester, in finely divided condition, to stand in a closed flask in the cold with a half-saturated solution of sodium ethylate for twelve hours. Although this method was originally proposed for the saponification of cellulose benzoates and acetosulfates, R. Woodbridge [1] has obtained best results by allowing the mixture of cellulose ester and ethylate to stand for sixteen hours in the cold with an excess of a solution prepared by dissolving 23 grms. metallic sodium in two liters of 95% ethyl-alcohol, the only caution required being that the saponification solution should be used in adequate excess, preferably about double the quantity theoretically required.[2]

In camphor containing plastics, the camphor may be separated by dissolving the plastic in acetone and precipitation with water, the camphor being afterwards extracted from the dried residue by means of benzene, amyl alcohol or amyl acetate. The difference between the original weight and the amyl alcohol-insoluble residue being camphor. In the estimation of camphor substitutes the same method may be followed, selecting for the extraction a solvent of the camphor substitute, which at the same time is a non-solvent of the cellulose ester. In acetate lacquers and bronzing liquids the ester may be determined by precipitation of the solution by water,

1. J.A.C.S. 1909, **31**, 1068; abst. J.C.S. 1909, **96**, i, 768; C.A. 1910, **4**, 667.

2. H. Mork (J.A.C.S. 1909, **31**, 1069) reports that errors in the method of saponification with alcoholic potash in the usual manner, attributable to the fact that boiling aqueous-alcoholic potassium hydroxide solution is accompanied by the production of acids at the expense of the cellulose residue, may be overcome by dilution of the saponifying mixture with water. He finds that with the ordinary cellulose triacetate, the suitable proportions are one volume each of alcohol and water, complete saponification being effected by boiling the ester with a half-normal solution of this character for one hour, when correct values are obtained.

benzine or benzene. If the presence of small amounts of resins, as copal, is suspected, hot amyl alcohol may be employed as precipitant, when the resin will remain in solution in the amyl alcohol and may be determined therein by simple evaporation to dryness.

(d) Method of H. Barthelemy.[1] According to a carefully worked out method of this chemist, acetyl groups in acetated cellulose may be determined in the following manner:

In this method the error limit lies within about 0.5%. Two gms. of well comminuted material are placed in an Erlenmeyer flask of 200 cc. capacity. By means of a pipette 40 ccm. normal soda solution is added and the flask well stoppered with a cork through which a glass tubing passes. This is provided with a rubber cap containing a longitudinal incision, which will permit the air to escape, but prevents the entering of air into the flask. The Erlenmeyer flask is placed in a drying oven, kept at a temperature of 85 to 90°, the contents shaken up three or four times every four hours and left in the oven until the following morning. After 16 hours, which is sufficient for a complete saponification, the contents of the Erlenmeyer is transferred to a graduated flask and filled up to 250 cc. The excess of soda is titrated in 50 cc. of the solution with 1/5 normal sulfuric acid, using phenolphthalein or congo red as indicator. It is advisable to check the change of color by titrating back with 1/5 normal soda solution, because the yellow color, which the solution acquires during saponification, makes it somewhat difficult to observe sharply the change of color. Supposing n cc. 1/5 N.-sulfuric acid were required to effect the change of color, the following equation holds good:

$$\frac{\left[40 \text{ cc} - \frac{\text{n. cc} \times 250}{5 \times 50}\right] \times 43 \times 100}{1000 \times 2 \text{ g}} = (CH_3\text{-}CO)\%;$$

1. Mon. Sci. 1913, 78, 549; abst. Kunst. 1913, 8, 412; C.A. 1913, 7, 3837.

C. Schwalbe triturates from three to five grms. of the material to be examined with 50cc. of a 25% solution of potassium hydroxide, allowing the mixture to stand in a closed flask for 48 hours. The solution is then diluted and neutralized with sulfuric acid. After standing for some hours the precipitated cellulose is filtered off, thoroughly washed, and the acetic acid in the solution obtained by steam distillation, as explained above.

In accordance with the (CH_3-CO) content found, the cellulose acetates may be classified as indicated in the following table:

Acetyl-Celluloses	Formulae	Acetyl Percent
Cellulose-Monoacetate	$C_{12}H_{19}O_{10}$ $(CH_3CO)_1$	11.75
" Diacetate	$C_{12}H_{18}O_{10}$ $(CH_3CO)_2$	21.08
" Triacetate	$C_{12}H_{17}O_{10}$ $(CH_3CO)_3$	28.67
" Tetracetate	$C_{12}H_{16}O_{10}$ $(CH_3CO)_4$	34.96
" Pentacetate	$C_{12}H_{15}O_{10}$ $(CH_3CO)_5$	40.26
" Hexoacetate	$C_{12}H_{14}O_{10}$ $(CH_3CO)_6$	44.80
" Heptacetate	$C_{12}H_{13}O_{10}$ $(CH_3CO)_7$	48.70
" Octoacetate	$C_{12}H_{12}O_{10}$ $(CH_3CO)_8$	52.12

In classifying an acetylcellulose according to the analytical results obtained, it is of course necessary in each instance to ascertain whether the cellulose acetate contains other acid radicals, and whether it is possessed of too great a reducing power towards Pasteur's or Fehling's solution.

Modification of O. Eberstadt.[1] This chemist has carefully studied the details of the Ost Method for the determination of acetyl in cellulose acetate, and has found that by previously swelling the acetated cellulose by a mixture of equal parts of water and alcohol or acetone and alcohol, subsequent saponification is greatly facilitated from the increased porosity of the cellulose ester. The sample—about one gram—is thoroughly soaked in the swelling medium in an Erlenmeyr flask, and to this is added exactly 100 cc. half normal potassium hydroxide. This is stoppered and heated at 25° with occasional shaking. The temperature greatly effects the rapidity of the saponification, increasing with an increase of temperature. Due to the fact that the cellulose absorbs free KOH, titration of aliquot portions withdrawn lead to erroneous results. Most satisfactory results are to be obtained by withdrawing from the flask containing the 100 cc. KOH and the sample, 50 cc. with a pipette which is titrated with normal HCl. The alkali remaining in the flask is then titrated. With phenol-phthalein as indicator, after the pink color disappears it can be made to return again by vigorous shaking of the flask, the absorbed alkali in the cellulose being washed out by the agitation. Finally, when the solution remains colorless upon repeated shaking, calculation is made in the usual manner. If the

1. Dissertation, Ueber Acetylcellulose, Heidelberg, 1909.

sample used has not been previously deprived of its moisture, allowance for this must be made in the final calculation.

Determination of Combined Sulfuric Acid. Where sulfuric acid or metallic sulfates have been used as catalysts, a small but variable amout of sulfuric acid enters the acetate product. These sulfonates undoubtedly exert a marked influence upon the stability and keeping qualities of the ester. The sulfuric caid may be estimated by one of the following two methods:

(a) About one gram of the finely comminuted and dried substance is thoroughly mixed with 1.5 gm. potassium nitrate and 5 gm. dry sodium carbonate, the mixture being slowly warmed in a crucible of ample size, and gently ignited. The mass is then dissolved in water, acidified with nitric acid and precipitated in the usual manner with barium chloride, washed and ignited.

(b) About one gram of the previously dried substance, preferably in the form of a fine powder, is warmed with fuming nitric acid in a covered crucible, the nitric acid being afterwards carefully evaporated off. 20-25 cc. aqua regia is next added, gently heated and the acid removed as before, by evaporation. This solution when diluted with water should be clear, otherwise the results will be inaccurate. The clear solution is precipitated with barium chloride in the usual manner, the barium sulfate being ignited and weighed.

CHAPTER VI.

APPENDIX.

Jesse Gutsch in 1913 contributed a dissertation upon the catalytic effects of the acetylation of starch and cellulose with acetic anhydride, which was based upon more complete and exhaustive experimentation than previous contributions. He apparently conclusively proved that acetylation without catalyst early departs from the normal course. The importance of this investigation and the conclusions reached, it is believed, justifies publishing herewith a practically complete free-hand translation of the results obtained.

According to Skraup [1] superficial or incomplete acetylation of starch with a small amount of sulfuric acid and a proportionally lower temperature gives rise to an acetyl compound, which when saponified with alkalis leads to a product possessing the most important qualities of soluble starch. If the starch is acetylated with considerable sulfuric acid, a substance or substances form which reduce Fehling's solution and are colored by iodine. There is, therefore, a splitting off, similar to the catalytic process occurring upon the addition of acetic anhydride, which Skraup [2] has designated as "acetolysis."

According to Traquair [3] in the acetylation of starch, the amount of acetic acid combining with the starch is continually increasing gradually, and not by definitely characterized steps. The solubility of partially acetylated starch is, as he says, a consequence of hydrolysis. In order to obtain an idea of the size of the starch molecule, Skraup [4] acetylized dry starch with acetic anhydride containing hydrochloric acid, whereby chlor-

1. Ber. 1899, **32**, 2413.
2. Monats. 1905, **26**, 1416.
3. J.S.C.I. 1909, **28**, 288.
4. Monats. 1905, **26**, 1415.

acetyl derivatives of starch were formed. Assuming that at least one chlorine atom was chemically combined, he obtained combustion numbers indicating the molecular weight of starch to be between 1700 and 1800. It was assumed, but not proven, that the product obtained was a uniform chemical compound.

The acetylation of cellulose may be divided into the two processes of (a) acetylation with acetyl chloride, and (b) with acetic acid anhydride.

In acetylation with acetyl chloride, after the discoveries of Franchimont, Cross and Bevan examined the subject exhaustively, their experiences being published in "Researches on Cellulose, 1895-1905." They acetylized hydrolyzed cellulose (mercerized cellulose), with acetyl chloride in the presence of zinc acetate,[1] or later with magnesium acetate[2] at temperatures below 30.°. The acetate so produced by them was considered as cellulose tetracetate $C_6H_6O_5(C_2H_3O)_4$. By the use of large quantities of zinc acetate (two equivalent weights) which Cross and Bevan used, they avoided, it is true, the "hydrolyzing-splitting" effect of the liberated hydrochloric acid, but not of the zinc chloride.

In order to better regulate the acetylation with zinc chloride, Henckel von Donnersmarck's Artificial Silk and Acetate Works[3] have recommended the addition of such solvents as nitrobenzene and *o*- and *p*-nitrotoluene. In order to eliminate the above described troublesome influence of the hydrochloric acid, Wohl[4] adds pyridine or quinoline. Where pyridine is used in large quantities, the temperature of acetylation may be elevated to as high as 150° without causing strong decomposition.

Boesch[5] acetylated viscose with acetyl chloride, while Althausse[6] employed acetyl chloride in the presence of sulfuric acid. When acetyl chloride is used, large quantities of

1. U.S.P. 530826, D.R.P. 85329. Chem. Centr. 1895, II, 268; J.S.C.I. 1895, 14, 496.
2. D.R.P. 86368; Chem. Centr. 1896, II, 567.
3. D.R.P. 105347; Chem. Centr. 1900, I, 271.
4. D.R.P. 139669; Chem. Centr. 1903, 1, 744.
5. U.S.P. 708456, 1902.
6. U.S.P. 692497, 1902.

hydrochloric acid gas are evolved which has to be neutralized, otherwise a strong hydrolyzing and chlorinating effect is observed, chlorine-containing cellulose acetates being formed. It therefore is not surprising that the use of acetyl chloride has fallen into disuse.

In the acetylation of cellulose in the presence of sulfuric acid, Skraup,[1] was the next after Franchimont to examine carefully the effect of the sulfuric acid. By "actylizing the cellulose energetically," a compound was obtained, which only "could have arisen by addition of anhydride." At first it was uncertain whether a pentacetyl derivative of a hexose, or a heptacetyl derivative of a hepta-valent alcohol was formed.

Franchimont[2] has stated that the quality of the acetylated products depends primarily upon the quantity of sulfuric acid used. Since Skraup and Franchimont have demonstrated how important a rôle the temperature and quantity of sulfuric acid plays, researches upon the acetylcelluloses have become more frequent. Lederer acetylized hydrocellulose with acetic anhydride and sulfuric acid and gives 70° as the preferred temperature of acetylation,[3] shortly afterwards advocating lowering the temperature to 30°.[4]

Miles[5] acetylized the cellulose with acetic anhydride in presence of sulfuric acid, at the same time hydrolyzing it by an elevated temperature. The Farb. v. F. Bayer & Co.[6] acetylized cellulose at 50°C. Lederer[7] observed that the copper numbers became higher and higher by long continued acetylation and by an elevated temperature. The Badische Anilin & Soda Fabrik[8] found that in the presence of certain quantities of water, the cellulose is acetylized more readily by means of sulfuric acid.

Skraup and Koenig[9] elevated the temperature of acetyla-

1. Ber. 1899, **32**, 2413.
2. Chem. Centr. 1900, I, 178.
3. D.R.P. 118538; E.P. 11164, 1902; F.P. 301749; U.S.P. 654988; Chem. Centr. 1901, I, 712.
4. D.R.P. 120713; F.P. 319848; Chem. Centr. 1901, I, 1219.
5. U.S.P. 733729.
6. D.R.P. 159524; Chem. Centr. 1905, II, 528.
7. D.R.P. 163316; Chem. Centr. 1905, II, 1301.
8. D.R.P. 184145.
9. Monats. **22**, 1011.

tion to 110-120° and obtained cellobiose octacetate. Jenks, Cross and Bevan [1] showed that when cellulose is nitrated or acetated, sulfuric acid enters the molecule in amounts depending upon the quantity of sulfuric acid used in the esterification. The Farb. v. F. Bayer & Co.[2] determined that, if much sulfuric acid is used, products are formed which become soluble in alcohol.

When it became known that by acetation as well as nitration of cellulose, sulfuric acid can enter the cellulose molecule, and that in consequence of this, due to the ready breaking down of these sulfates, decomposition of the cellulose ester is prone to occur, a remedy was looked for. In order to stabilize solutions of acetylcellulose which contain the acetosulfo group, Knoll & Co. add bases or salts of bases with weak acids to the solution containing the sulfuric acid.[3]

Haeussermann [4] has demonstrated that by the nitration of cellulose acetates, nitric acid can replace the acetic acid groups. The addition of nitrates to the unstable cellulose acetosulfates has perhaps a similar effect.— Because the decomposing action of the sulfuric acid cannot readily be overcome, it is difficult to obtain stable esters of normal or undecomposed acetylcellulose in this way. Other catalyzers have, therefore, been tried.

In acetylizing cellulose in the absence of sulfuric acid Vignon and Gerin acetylized both cellulose and oxycellulose in the presence of zinc chloride and boiling acetic anhydride. They describe the product formed as a cellulose tetracetate. In the past few years contact substances have been recommended, the following being found in the patent literature.

Aromatic sulfonic acids,[5] sulfinic acids,[6] halogen fatty

1. Ber. 1901, 34, 2496; 1905, 38, 3551.
2. D.R.P. 153350; Chem. Centr. 1904, II, 625.
3. D.R.P. 196730; F.P. 371357; F..P. 376578.
4. Chem. Ztg., 29, 667
5. U.S.P. 709922.
6. Knoll & Co., D.R.P. 180666, 180667.

acids,[1] monobasic mineral acids,[2] neutral salts of powerful acids,[3] and dimethylsulfate.[4] A summary of the different processes may be found in Zts. f. ang. Chem., 1906, page 993, and 1907, page 743.

In the reaction of acetic anhydride on organic compounds in the presence of catalyzers, Bertram,[5] Hubner,[6] Descude,[7] Geutner,[8] Thiele,[9] Freiss [10] and Rogow [11] have demonstrated that it is possible to acetylize various aldehydes by useing acetic acid anhydride with either sulfuric acid or zinc chloride. Knoevenagel [12] and his pupils have extended this field by useing other catalyzers, and have also acetated oxygen containing rings by splitting them.

Since it has become known that cellulose as well as starch by being hydrolyzed assumes the character of an aldehyd, it must be possible by selecting a suitable catalysator to acetylize the aldehyde group or groups. By the acetylation of different substances of a known molecular constitution, which contain an aldehyde oxygen atom with hydroxyl groups, it is possible by this parallel study to obtain a knowledge of the constitution of the cellulose and starch molecule. Such experiments are now being made in the laboratory of this place.

By the acetylation of cellulose, Cross and Bevan [13] thought they obtained pentacetate (on C_6). They supposed therefore that first by taking up water, two hydroxyl groups are formed from the aldehyd oxygen, which is then acetylised.

In the controversy between Cross and Bevan and Green about the most probable constitutional formula for cellulose,

1. Akt. Ges. f. Anilinfabrikation, D.R.P. 198842. Knoll & Co., D.R.P. 203462.
2 Knoll & Co., D.R.P. 201233; F.P. 319848; Monats. **26**, 1459.
3. Knoll & Co., D.R.P. 203178, 206950.
4. E.P. 9998, U.S.P. 826229.
5 Jour. prakt. Chem. (2), **49**, 1.
6. Zts. Chem. 1867, 277.
7. Bull. Soc. Chim. (3), **27**, 867.
8. Ann. **106**, 25.
9. Ann. **311**, 353.
10. Bull. Soc. Ind. Mulh. **69**, 44.
11. Ber. **34**, 3881.
12. Dissertation Jung. 1907. Dissertation Transier 1908;
13. Chem. News, **61**, 123. Chem. Centr. 1890, 712.

Green [1] speaks of a latent aldehyde group which can be acetylised. The object of this work was to study the influence of different catalyzers on the degree of the acetylation in order to contribute in this way data for clearing up the constitution of the starch and cellulose molecule.

In the acetation of starch and cellulose nine catalyzers have been studied, which decompose the starch and cellulose molecule much slower than the sulfuric acid. With every catalyzer one or several series of experiments were performed. It has been acetylised at the temperatures of 60, 80 and 100 degrees C. With every catalyzer the experiment was performed until the maximum of the acetyl number was obtained or until a decided decomposition of the starch and cellulose was apparent.

The decomposition could be easily recognized by the strong reduction of Fehling's solution.

After the saponification of the starch acetates with caustic potash and acidifying with hydrochloric acid, no blue coloring in case of decomposed starch was obtained by the addition of iodine solution.

In the case of acetylcellulose a more pronounced decomposition could always be recognized by a marked decrease of the viscosity of its solution.

Comparing the acetyl numbers to exact results cannot be expected. (See Special Part.) Ost [2] assumed, plus or minus, 2% acetic acid as the limit of exactness. The numbers which are side by side in the tables given below have been determined, with a few exceptions, in two independntly performed series of experiments, and correspond well. As the tables demonstrate, the difference of the rule is only some tenths of a percent.

1. Zts. Farb. u. Tertchem. **8**, 309.

2. For details of the coloring of artificial leather by treatment with colored nitrocellulose or acetylcellulose lacquers, consult E. Girzik, D.R.P. 281304, 1913; abst. Kunst. 1915, **5**, 21. For the manufacture of esters and ethers of ethylidene glycol and vinyl alcohol, see E.P. 14246, 1913; U.S.P. 1084581, 1914; abst. J.S.C.I., 1914, **33**, 219, 767. W. Lindsay (U.S.P. 1128468, 1915) prepares plastic masses by heating an acetone-soluble acetylcellulose with triphenyl phosphate in the presence of a small proportion of methyl alcohol.

All acetyl percents are calculated for $C_{12}H_{20}O_{10}$. The following table shows the theoretical numbers:

TABLE VI.

FORMULA	Acetate	% Acetyl	Yield of 5 gms. dry substance
$C_{12}H_{19}O_{10}(CH_3CO)$	Mono	11.75	5.7
$C_{12}H_{18}H_{10}(CH_3CO)_2$	Di	21.08	6.3
$C_{12}H_{17}O_{10}(CH_3CO)_3$	Tri	28.67	6.9
$C_{12}H_{16}O_{10}(CH_3CO)_4$	Tetra	34.96	7.6
$C_{12}H_{15}O_{10}(CH_3CO)_5$	Penta	40.26	8.2
$C_{12}H_{14}O_{10}(CH_3CO)_6$	Hexa	44.80	8.8

Acetates of Starch. Starch can be readily acetylated without the presence of catalyzers,[2] but the process then takes place very slowly. According to the older statements it is supposed glacial acetic acid and acetic acid anhydride give rise to a higher acetate as the hexacetate (on C_{12}) of the unchanged starch, but this cannot be obtained without the influence of the tried catalyzers (copper sulfate, trichloracetic acid, methylaminsulfate, potassium bisulfate, ferrous sulfate, disodium phosphate). By using methylaminsulfate as catalyzer in the case of starch, a proportionately strong decomposition takes place while the acetyl number rises. Also in other cases the acetyl numbers have passed beyond the theoretical number (44.8%).

(See Table III, 100 and 200 hours by using $CuSO_4+H_2O$; CCl_3COOH; $FeSO_4+H_2O$; and $KHSO_4$ as catalyzers.) That is not at all a new appearance. Skraup, who also acetylized starch with different catalyzers like sulfuric acid and hydrochloric acid, observed that even "at a mild acetylation" more acetyl is found than is calculated according to the Brutto formula.[1] This excess of acetyl can be supposed as a consequence of arising formic acid.

In the named cases after saponification with caustic potassium and acidifying with acetic acid, the blue colour showing the presence of starch is always obtained by iodine

1. Zts. Chem. 1869, 264; Amer. Chem. J. 5, 359.
2. Ber. 1899, 82, 2413.

in spite of the longer continuance of the acetylation. With methylaminsulfate it does not happen after a longer acetylation (Table II), but a brown colouring is obtained and at the same time the Fehling's solution is reduced, which is proof that the starch molecule has been changed in a certain degree. By using copper sulfate, Fehling's solution is also reduced after long continued acetylation.

It may be here mentioned also that other indications of the decomposition of the starch molecule can be observed in the named cases. These are diminution of the viscosity of the solutions as well as an increase of the dark colouring, when heated with caustic potash on the water bath.

On the whole it can be stated that the starch molecule is acetylised gradually, more until the hexacetate (on C_{12}) of starch is obtained, if acetic acid anhydride in presence of glacial acetic acid reacts with starch with or without catalyzers. Afterward the reaction stops without catalyzer or catalyzers of a mild effect. Under the influence of stronger acting catalyzers the starch molecule is then decomposed, being acetylized, and the acetyl number rises for some percent. A further acetylation and decomposition happens only in the case of methylaminsulfate.

It has been already mentioned that all are amorphous very hygroscopic white powders. Under the microscope the conversion of starch into the hexacetate can be observed; it can even approximately be judged from a microscopical examination how far the product has been acetylized. The granules of potato starch become from the outside always more opaque until gradually the light centre disappears; then the granules disintegrate and a microscopically fine, amorphous opaque powder results. Although with regard to appearance these acetates are very much alike, their behaviour toward solvents is very different. For the starch acetates the following solvents have been used: water, absolute alcohol, ether, chloroform, acetone, acetic ester and glacial acetic acid. All examined starch acetates are insoluble in ether and absolute alcohol. On the whole they can be said to be insoluble also in

water. But if the acetyl number is under 7% they are also soluble in water.

The best of the tried solvents for starch acetates is certainly chloroform.

We consider now the different series of experiments.

Since in the absence of catalyzers, acetation occurs more slowly, opportunity was offered of studying the lower products of acetation. It was found for these products that the solubility in water quickly disappears when the acetated product contains about 12% of acetyl, while the solubility in chloroform increases.

The end product is always insoluble in water and easily soluble in chloroform. The same is the case with acetic acid, but the latter is not quite such a good solvent as chloroform. Acetic ester and acetone have an equal solvent power, but much less than the above named solvents.

At a temperature of 80° C. acetylation takes place very slowly. Even after 200 hours only 17.6% acetyl are obtained. The starch is not dissolved. Examination with iodine under the microscope shows the presence of unchanged starch.

At 100° C. the reaction occurs much more quickly. After 100 hours it is nearly finished (43.1%) and after 200 hours the hexacetate (44.8%) is obtained. By this acetylation with acetic acid anhydride in presence of glacial acetic acid the starch gradually becomes dissolved, and after 20 hours a complete solution is obtained. At the same time the reaction for starch disappears. After saponification with caustic potash the reaction for starch can always readily be demonstrated as well as with all higher acetylised products. All these acetates give after saponification with caustic potash on the water-bath, a slight yellow color. Fehling's solution does not become reduced and the viscosity of the mixture of the acetylation is a very great one. We may therefore suppose that the end product is a hexacetate of starch.

Starch is much more readily acetylized under the influence of copper sulfate. At 80° C. the hexacetate is obtained after 50 hours. The acetyl numbers for 50, 100 and 200 hours are

higher than the theoretical number of the hexacetate (44.8%). At the same time Fehling's solution is reduced and by saponifying with caustic potash dark colored products (partially resins) are obtained. Although after saponification the proof with iodine is a positive one, it can be supposed that the starch molecule has begun to disintegrate. The typical behaviour with solvents can be found here again; also the corresponding high viscosity is here, if the temperature and the continuance of the reaction is taken rightly.

The catalytic influence of trichloracetic acid seems to be small. This acid has but little decomposing effect on the acid molecule, for, even after an acetation of 200 hours at 100° C., the product is without effect upon Fehling's solution. The addition of iodine after saponification with caustic potash gives always a clear blue color, and upon saponification with caustic potash on the water-bath, a light yellow color. The viscosity of the products of reaction is very great. In one experiment performed with trichloracetic acid made to determine the effect of larger quantities of the catalyzer, the product formed, contained after 50 hours, but 26.2% acetyl. (By the saponification with KOH, 26%, and by distillation with sulfuric acid, 26.4%. It would therefore appear that larger quantities of trichloracetic acid has an inhibiting, rather than an accelerating effect. It should be noted that the chloroform solutions in this series are often only pseudo-solutions, especially at 80° C.

Of all the catalyzers examined, none has a more remarkable influence upon starch than methylaminsulfate, under the influence of which acetation progresses very quickly. Methylaminsulfate has not only an accelerating effect on the acetation, but at the same time it has also a strong splitting effect on the acid molecule. At 80° C. the reaction can very well be observed. That the decomposition takes place at the same time as the acetylation appears probable from the results obtained. Before the hexacetate is reached and before the starch is dissolved Fehling's solution is reduced. The yield does not reach approximately the theoretical number for a

hexacetate. If acetylized a longer time the yield of products incoluble in alcohol decreases more and more, so that after 50, 100 and 200 hours at 100° C. no precipitate was obtained by adding absolute alcohol. The reduction of Fehling's solution also constantly increases. The acetyl numbers are much higher, even of the alcohol insoluble products than the limit number of a hexacetate. Numbers up to 52.2% were obtained. This is the theoretical number of an octacetate. But this octacetate is not an octacetate of starch, because after being saponified with caustic potash a red-brown colouring is obtained with iodine in a neutral or a weak hydrochloric acid solution (corresponding to the dextrins). Upon saponification on the water-bath with caustic potash only a dark colored solution is obtained and many resins appear.

The black alcoholic solutions of experiments 50, 51 and 52 after evaporiation on the water-bath gave black, sticky products of a weight of 1.1, 1.6 and 4.5 gym. Acetyl determinations of these residues gave the surprising result that they contained only 19.9%, 11.0% and 14.3% acetyl. These results are not exact, because the sticky mass in thin layers in spite of being dried two days always smelled of acetic acid. These residues were easily soluble in water and reduced Fehling's solution. Saponified with caustic potash they gave a yellow-brown colouring and did not give a precipitate with phenylhydrazine.

In order to obtain these products of decomposition a larger experiment was performed with ten times as much (50 gm.) as the usual quantity, the starch being heated with acetic acid anhydride, glacial acetic acid and methylaminesulfate during 300 hours at 80° C. (without being stirred). The black, thin-flowing solution was precipitated with alcohol in order to precipitate the formed acetates (20.5 gm.). This product from the precipitation contained 49.8% acetyl (after the method of saponification with caustic potash 50.2%).

This product was saponified with caustic potash and gave brown color. The test with iodine of the saponified substance gave also a brown color. Fehling's solution was strongly reduced.

The filtrate from which the acetates had been precipitated by alcohol was evaporated on the water-bath. The black viscous residue was dissolved in water (easily soluble) and sulfuric acid was added. This solution was distilled with steam. Saponification of the acetates took place and acetic acid and other volatile elements distilled over. From the distillate nothing could be precipitated with potash.

The solution in the retort had separated insoluble products and was filtered. The residue on the filter (8.2 gm.) was black and reduced Fehling's solution. Boiled with caustic potash a yellow-brown dyed solution was obtained. In water the substance is insoluble, but swells very much. The solution was separated from the residue (8.2 gm.), made distinctly alkaline, saturated with carbonic acid and evaporated on the water-bath until dry. The firm black mass was mixed with fine, pure quartz and was extracted with absolute alcohol in the Soxhlet apparatus. In this way the potassium salts of the organic acids not volatile with steam, which might be formed from the acetylstarch, were separated from the sugars and potassium sulfate.

Like trichloracetic acid, potassium bisulfate has but little accelerating effect. At 100° C. it requires between 50 and 100 hours before the end product is obtained. Although these acetates did not reduce Fehling's solution and the yields remain relatively high, a slo wacetolytic splitting seems to happen, as shown by a decrease in viscosity. As usual, the starch is gradually dissolved and a solid, light yellow, tough mass is obtained. This clear mass is rather constant, but after 100 hours becomes liquid and after 200 hours a thick, viscous solution results, which shows a dark color.

At 100° C. an experiment was performed, where the mixture consisted of 10 gm. starch, 10 gm. potassium bisulfate and 50 gm. glacial acetic acid. It was acetylized 16 hours. The product contained 18.5% acetyl and can be compared with experiment 12. But the solubilities were very different. It was insoluble in ether, partially soluble in alcohol and chloroform, hardly soluble in acetone and acetic ester, soluble in acetic acid and easily soluble in water. It strongly reduced

Fehling's solution. After being saponified with caustic potash, the test with iodine showed a yellow, later on a brown color; saponified with caustic potash on the water-bath, a dark yellow color. Tannic acid gave no precipitate. Phenylhydrazine gave a precipitate, which was decomposed upon boiling. It is a typical dextrin-acetate.

An experiment with 0.5 gm. stannous chloride and 0.5 gm. potassium bisulfate as contact substances gave after 23 hours at 100° C. a light yellow viscous solution. The acetate contained 45.6% acetyl and was a normal hexacetate. It was insoluble in water, alcohol and ether, solduble in chloroform, acetic ester, acetone and glacial acetic acid. Fehling's solution was not reduced. After being saponified the test with iodine showed blue.

The effect of ferrous sulfate can be very well compared with the effect of copper sulfate. Ferrous sulfate has not quite such an accelerating effect, but otherwise the acetates obtained are very much alike. The end product of the acetylation is obtained after about 50 hours at 100° C. Since these products become sticky with water and can not be filtered, the ferrous sulfate could not be washed out of the starch acetates. It was therefore not possible to use Fehling's solution in order to examine for reduction. The viscosity of these acetates in the mixture of the acetylation corresponds with that of copper sulfate.

After having used as catalysators an acid, an acid salt and a salt in which the metal can easily change its degree of value, an "alcalic" reacting salt was applied. As such one disodium phosphate was chosen. The result was that this salt has almost no delaying effect on the acetylation. A decomposition of the starch molecule does not occur.

Traquair[1] obtained a substance, to which he gave the name "Feculose." This acetate is supposed to serve as dressing purposes. It is superficially acetylized and soluble in water.

With disodium phosphate in experiments 18, 19 and 20 similar products were obtained. An experiment was made at

1. Zts. ang. Chem. 1909, 2346.

60° C. (No. 78), the mixture of the acetylation containing 44 gm. glacial acetic acid and only 1 gm. acetic acid anhydride. It was acetylized 100 hours. The product contained 5.8% acetyl. If the anhydride had been entirely used up, the substance would contain 8.6% acetyl. The product is particularly easily soluble in water and gives a clear viscous solution. After standing a longer time the solution does not become gelatinous.. The complete solubility in water seems to follow the use of the sodium phosphate. In the series of experiments without satalyzer (No. 56) with an excess of acetic acid anhydride a product was obtained in a short time, which was not quite so easily soluble in water. It cannot be determined whether 6.0% acetyl is essential for the solubility or not. The acetate can be considered as monoacetate on C_{24}). (Theoretically 6.2% acetyl obtained No. 78: 5.8%, and No. 19: 6.1%.)

It was more difficult to determine the yield of the starch acetates than that of the cellulose acetates. The products absorbed water very readily, and made washing and filtration difficult. In most cases on account of the catalyzers a roughly determinable factor of correction for the ash had to be applied. From Tables V and VI it can be seen that the yield in most cases is smaller than the theoretically calculated quantity. In the experiments in which decomposition appeared, the yield was still smaller, because the products of decomposition are soluble in absolute alcohol. This can be seen particularly distinctly in the series of experiments with methylaminesulfate.

It has been found much more difficult to determine the acetyl number of the cellulose acetates than of the starch acetates.

In spite of that I succeeded in working out also for the cellulose acetates a method for the determination of acetyl, by means of which many acetyl determinations could easily be performed at one time and which is more exact than the methods proposed up to the present. In order to acetylise the cellulose, three series of experiments were made, that os with stannous chloride, ammonium persulfate and pyridine sulfate. Ferrous sulfate and disodium phosphate, which had

been used for acetylizing the starch, were not applied as catalyzers for cellulose.

We saw that for the acetylization of starch the catalyzers had a more or less accelerating effect and that the starch molecule could not be burst easily; methylamine sulfate was the only exception.

In the case of cellulose it is different. If acetated under the same conditions as starch, the cellulose is acetylized quicker, but after having the hexacetate (on C_{12}), a strong decomposition of the cellulose molecule commences (Tables IX, X, XI and XII).

The stability of the starch molecule compared with that of the cellulose molecule by acetylation is striking, because by boiling with diluted aqueous acids and by being treated with diastase, starch is much easier hydrolyzed than cellulose.

Signs of the decomposition of the cellulose are:

1. Dark color of the mixture of the acetation.

2. Darkening when the acetate is boiled with potassium hydroxide.

3. Reduction of Fehling's solution.

4. Strong diminution of viscosity of the mixture of acetation.

As acetation proceeds, the solution becomes darker and less viscous, until at last a black, thin solution is obtained. According to the catalyzer used, decomposition of the cellulose molecule proceeds with greater or less rapidity. Results with cellulose are comparable with starch in that methylamine sulfate is the most effectual catalyst examined (copper sulfate, trichloracetic acid, and potassium bisulfate). In the case of starch, no decomposition with trichloracetic acid, or disodium phosphate was observed, and but little with copper or ferrous sulfates. In the latter instance, decomposition of the starch is only observable after long-continued acetation. In the case of cellulose, long acetation with or without catalyst always gives rise to decomposition at elevated temperatures.

In order to determine that decomposition quantitatively, the value of the reduction with Fehling's solution (copper

number) and the viscosity of the solutions which had been obtained directly by the acetylation, were found. The exactness of the determination of the copper number can be supposed to be 0.5%. Schwalbe [1] states the values of the reduction of the different celluloses, oxycelluloses and hydrocelluloses against Fehling's solution in percents of copper. The same principle is pursued also here.

A further essential difference between the acetylation of cellulose and starch is the physical nature of the acetate obtained. From starch a fine, amorphous, snow-white, strongly hygroscopic powder is always obtained.

The behavior of the cellulose acetates with hot caustic potash corresponds with that of the starch acetates. These cellulose acetates, which reduce Fehling's solution, from about 6.3% copper, give by being heated with caustic potash on the water-bath yellow-brown to yellow colored products. It is not possible, as with starch, to observe the process of acetylation through the microscope.

Referring to their behavior against solvents, the cellulose acetates resemble more the starch acetates. Also here all acetates were insoluble in water, absolute alcohol and ether. Chloroform is also here the best solvent, then acetic acid, acetone, and acetic ester.

With trichloracetic acid (experiment 131) and methylaminsulfate (No. 132) two experiments were made in order to study the influence of the quantity of the catalysator. Both experiments were acetylized 50 hours at 80° C. with 5.0 gm. instead of 0.5 gm. catalyzer as usual.

Trichloracetic acid. The comparison of experiment No. 103 with experiment 131 demonstrates that the acetylation with much trichloracetic acid does not take place in the same way. The obtained acetyl numbers are:

Experiment	Trichloracetic Acid	Time	% Acetyl
103	0.5 g.	50 hours	43.5
131	5.0 g.	50 "	47.5

No. 31 is a little more soluble in acetic ester, acetone and glacial actic acid than No. 103.

1. Ber. 1907, 40, 1347.

Methylamine sulfate. If methylamine sulfate is used in large quantities, acetylation is delayed, due to the decomposition.

Experiment	Methylaminesulfate	Acetyl	Time	Copper No.
108	0.5 g.	49.1	50 hours	12.6
132	5.0 g.	42.7	50 "	19.9

The condition of the solubility of both acetyl products are approximately equal.

Since the other examined catalysts have not been soluble in larger quantities, corresponding experiments could not be performed.

There is probably no reaction, which has been so long and thoroughly studied, as the nitration of cellulose. In spite of the long time, the pains and expense spent for this interesting process partly on account of the scientific, party on account of technical interests, the exact constitution of cellulose has remained unknown. First now it seems possible to obtain better knowledge of the cellulose molecule by means of the acetylation of cellulose. It is therefore interesting to compare the process of nitration with that of the acetylation.

In the nitration of cellulose usually a mixture of sulfuric acid and nitric acid is used. Formerly the sulfuric acid was believed to act only as a water-depriving substance. In the case of the acetylation of cellulose, Franchimont's experiments [1] demonstrated distinctly that the sulfuric acid has catalytic effect. With the nitration of cellulose the exact proof of this has not been demonstrated. The sulfo-compounds of the polyhydroxyl containing compounds are mostly readily decomposable, for instance glycerol sulfuric acid and cellulose sulfuric acid. The technically produced nitrates of the cellulose must react perfectly neutral. If they are not neutral, they contain sulfuric acid in form of acid esters and decompose them, easily developing nitrous vapors. When such sulfuric acid containing products in larger quantities are present in the nitrocelluloses, the decomposition frequently takes place in the form of an explosion.

1. Ber. 1879, **12**, 1941; Compt. rend. **89**, 711.

Another reason for supposing bound sulphuric acid in the production of the nitrocelluloses is the following: It is a known fact that the cellulose nitrates can be made free from the last traces of the nitrating acid only with great difficulty. If it is washed with cold water about 2% sulfuric acid remains in the fiber. But if the same nitrate is treated with steam or diluted sulfuric acid or potash, it is possible to obtain a neutral, stable product. Similar observations have been made with the nitration of glycerol.

Cross, Bevan and Jenks [1] claim to have isolated even the neutral nitrocellulose sulfuric acid esters and acetocellulose sulfuric acid esters. They attribute to these esters, as it seems to me, very doubtful quality, that they are remarkably constant against alkaline saponification, but very sensitive against water.[2]

If cellulose treated with a mixture of acetic acid anhydrid and nitric acid, according to Smith and Berl,[3] only nitrates of cellulose are obtained. The nitrating effect of the mixture is the stronger, the more acetic anhydride contained in it.

Many of the catalysts used for the acetylation of cellulose contain sulfuric acid. It has therefore been determined as to whether the obtained acetates also contained sulfuric acid. Where qualitatively sulfuric acid could be proved, quantitative analyses were made. It will be shown below that not all acetates contain sulfuric acid. It is not at all probable that this sulfuric acid adheres only mechanically to the acetylcellulose, since all acetates after being precipitated by water have been thoroughly washed in cold running water. The acetates, which were obtained by means of copper sulfate, were always free from sulfate, because highly acetylized products were always obtained. It is different in the series of experiments with methylaminsulfate, potassium bisulfate and ammonium persulfate. In the last three series some, but not all, of the products contain sulfate. Also the quantitative results are interesting.

1. Ber. 1901, **34**, 2496.
2. Ber. 1905, **38**, 1859.
3. Ber. 1908, **41**, 1837.

The sulfuric acid increases gradually to a limit value and then gradually decreases and disappears entirely at the hexacetate stage.[1] All hexacetates produced with a sulfuric acid containing catalysts were free from sulfate. The sulfate contaning acetates carbonize when dried in the vacuum at 100° C. and had to be dried therefore at a low temperature). Cross and Bevan [2] found similar results with acetocellulose sulfates. In the series of experiments with potassium bisulfate the solution at 38.2% acetyl (No. 122) is almost a complete one; but by using stannous chloride at 36.5% acetyl (No. 116) even the fiber of the cellulose still exists. It is remarkable that, as soon as sulfuric acid esters of cellulose are formed, Fehling's solution is reduced, even if the cellulose is not yet dissolved (compare the potassium bisulfate and methylaminsulfate series).

By the use of a mixture of nitric and sulfuric acid, the maximum limit of nitration is, according to Guttmann, 13.92% N., and according to Lunge and Weintraub,[3] 13.87% N. Hoitsema [4] nitrated in the presence of phosphorus pentoxide instead of sulfuric acid and obtained 14.0% of nitrogen. But these highly nitrated products are unstable, and readily decompose with a loss of nitrogen. The theoretical nitrogen percentage for a hexa-nitrate (on C_{12}) is 14.16. Should the cellulose molecule contain six hydroxyl groups, the combination with nitric acid is not stable, as evidenced by the proneness to decomposition. Will [5] attributes the decomposition of highly nitrated cellulose to the presence of small amounts of unknown substances, which catalytically decompose the nitrocellulose and transport it in a "limited state." Depending upon the temperature and degree of nitration of the original nitrate is the time and nitrogen percentage that this period of equilibrium appears.

When the acetyl numbers in tables IX and X are com-

1. Ber. 1905, **38**, 3539.
2. Ber. 1905, **38**, 1859.
3. Zts. ang. Chem. 1899, 144.
4. Zts. ang. Chem. 1898, 173.
5. Escales, Die Schiesbaumwolle, 171-177.

pared it is seen that numbers were obtained, which far exceed the hexacetate. How can these high acetyl numbers be explained?

Vignon and Gerin have proven that the cellulose nitrates are aldehydes and therefore have reducing effect on Fehling's solution. The tables demonstrate the same for the cellulose acetates.

It is known to be possible by using various catalysts to acetylize the most varied aldehydes and to produce the corresponding diacetyl compounds. For instance with lineol a "bridge-oxygen" can be burst and acetylized. A particularly suitable catalyst in the case of lineol is anhydrous ferric chloride.[1]

By assuming the presence of one or several aldehyde groups the high acetyl numbers could be explained. For in the series of experiments without catalyst, with copper sulfate, trichloracetic acid, potassium bisulfate and stannous chloride the number does not exceed the hexacetate. Only by using methylaminesulfate and ammonium persulfate very much higher numbers were obtained, previously observed by Skraup [2] with sulfuric acid, and in the laboratory of this place with sulfuric acid and ferric chloride. From Table XV it is seen that, as soon as these very high numbers are obtained the yield decreases in consequence of the solubility in water of acetylized products of the decomposition. This aldehyde group (or groups) must be latent, for why do not many lower acetylized celluloses and cellulose itself reduce Fehling's solution? By determining the copper numbers quantitatively I could discover certain facts. It is striking how often the number 6.3%+0.5% and a multiple of this number was obtained. The opening of the aldehyde groups does not appear in a continually progressing reaction, but seems to show certain "stooping" points. This appearance results distinctly from the copper numbers, which by using as catalysts copper sulfate, potassium bisulfate (6.3+) and methylamine sulfate (6.3% and 12.6%) were obtained. As long as the copper

1. Dissertation Transler, Heidelberg, 1907.
2. Ber. 1899, 32, 2413.

number fluctuates around 6.3+, the viscosity remains proportionally higher, but as soon as the double number 12.6% is reached, the viscosity rapidly decreases.

As long as the copper number remains under 6.3%, the acetate after being precipitated with water is always colloidal (assuming the cellulose is sufficiently acetated to dissolve in the acetylating mixture), but as soon as the higher copper numbers are reached the cellulose acetate is precipitated as a powder. Schwalbe obtained from oxycellulose 5.6%.[1] Vignon[2] studied the quantitative reduction with Fehling's Solution on nitrocellulose. He also obtained similar stopping points, and states that the reduction is not dependent upon the degree of nitration ,and is the same both for nitrocellulose and nitroxycellulose. The copper number for the various sugars was obtained empirically.

Cross and Bevan draw he inference[3] that 6.3% copper corresponds with a free aldehyde group and that the cellulose molecule is $C_{24}H_{40}O_{20}$. I have come to the conclusion that at least two aldehyde groups have to be ruptured in the acetylized products, which give copper numbers as high as 12.6%, for by acetation with these catalyzers (for instance methylamine sulfate), two stopping points in the copper numbers (6.3% and 12.6%) are observed.

Upon further progression of the acetylation the acetyl and copper numbers increase accordingly, the yield and viscosity meanwhile decreasing to a minimum. The same point, however, is not again obtained. It merely happened that in the series of experiments with methylamine sulfate, the last number is the eighth multiple of 6.3%, i. e., 50.7%. It is doubtful if numbers in excess of 12.6% represent an unacted upon cellulose molecule. In experiments of this nature, the products of saponification of the acetates with potassium hydroxide are found to be soluble in water, showing much decomposition of the acetate.

Whether the aldehyde group first freed is acetated at

1. Ber. 1907, **40**, 1347.
2. Bull. Soc. Chim. (3), **25**, 130.
3. Researches on Cellulose, 1895-1905.

once depends upon the most varying factors. One catalyzer (as potassium bisulfate) may more favor a decomposition, while another (as trichloracetic acid) may increase acetylation. Also the reaction with the same catalyzer at different temperatures may cause the aldehyde group to be either split off or acetated.

For an acetic ester in which twelve hydroxyl groups (on a C_{24} molecule) one aldehyde group is acetated, theory requiring 48.7% acetyl. In those instances where acetation and decomposition progress simultaneously and quickly, as with methylamine and ammonium persulfate, the acetation of the first aldehyde group is complete as soon as the copper number rises to 12.6%.

Copper sulfate appears to be particularly adapted to the acetation of aldehyde groups, although in other cases copper sulfate alone has proven particularly efficient for acetating aldehyde groups.

If, during acetylation, decomposition of the cellulose molecule soon occurs, as with methylamine sulfate and ammonium sulfate catalysts, the viscosity constantly decreases. With little decomposition, the viscosity increases, and where the viscosity decreases are at those points where the copper numbers remain stationary. Where the copper number remains below 6.3%, the viscosity varies within two maxima. This may be explained, perhaps, by the appearance of secondary reactions, by condensations or isomerism. The solutions obtained when copper sulfate was used as a catalyst, are granular. Where the copper number exceeds 6.3%, a marked decrease in viscosity takes place.

In the presence of pyridine as catalyst, all cellulose acetates produced contain sulfates, which increase in percentage with added amounts of catalyst. When these acetates are boiled with caustic potash, the odor of pyridine is noticeable, and increases with increase of sulfuric acid in the acetated product. All these acetates are insoluble in absolute alcohol, ether, chloroform, ethyl acetate and acetone.

With small quantities of neutral pyridine sulfate, acetylation takes place very slowly, 200 hours acetation at 80° C.

being insufficient time to completely dissolve the cellulose, which still retained the morphological structure of the cotton filament. The products are insoluble in water and glacial acetic acid. The sulfuric acid content appears to decrease with increasing acetyl number. Upon saponification of the cellulose acetosulfates insoluble and soluble in glacial acetic acid, dark brown colored products arise, without the separation of cellulose. In consequence of the solubility of these bodies and of their products of saponification in water, and their brown appearance upon saponification, it is assumed they are pyridine salts of acetated dextrin-sulfuric acids. The fact that there is no reduction of Fehling's solution does not contradict the existing literature.

The acetylations were performed in a thermostat with mechanical stirrer. The quantities of material employed were 5 gm. dried starch or cellulose, 20 gm. glacial acetic acid, 25 gm. acetic anhydride and 0.5 gm. catalyst. The acid and anhydride were free from sulfuric and hydrochloric acids, the acetic anhydride being distilled before use. The cellulose was acetated in small closed containers of about 80 cc. capacity, heated in the thermostat, which was closed by a collodion-covered cork stopper. Where cellulose was acetated without catalyst at 80% C. the cellulose dissolved after 45 hours upon stirring, and without stirring immersion for 60 hours was required to produce a homogeneous solution. Acetylated starch was precipitated by absolute alcohol and washed to neutrality. Where water or dilute alcohol is used, a colloidal mass is formed, almost impossible of filtration. Absolute alcohol or other anhydrous solvent admits of the precipitation of a finely granular product, the alcohol being finally replaced by ether, and this eventually removed by evaporation on the water-bath. A slow current of air facilitates drying. In the solubility determinations, it was found that whereas the cellulose acetates dissolved but slowly, the starch acetates passed into solution with great rapidity.

In the determination of acetyl in starch acetate, the principle of Perkins' method (Jour. Chem. Soc. 89, 811) was fol-

lowed with satisfactory results; 2 gms. being stirred up with 25 cc. water and 25 cc. alcohol until the mass had swelled (about 15 min.). 50 cc. aqueous potassium hydroxide containing 9 gms. KOH was added, water-bath heat applied until entire solution (usually about 3 hours). To this solution at least 45 gms. of 20% sulfuric acid was next added and the mixture steam distilled. Highly acetylated products require a longer period of saponification. Caustic potash saponification has been found to yield numbers often higher than where sodium hydroxide has been used as the alkali. Best results were obtained with the method of Eberstadt (page 2925).

The general results are summarized in the following tables:

TABLE VII.

ACETYLATION OF STARCH

PERCENTAGE OF ACETYL

Time	Without Catalyst	Copper Sulfate	Trichloracetic Acid	Methylamine Sulfate	Acid Potassium Sulfate	Ferrous Sulfate	Disodium Phosphate
					Acetylating Temperature 100°C.		
2 hrs.	.....	.....	7.0	.....	.....	.....	2.5
5 "	11.2, 11.9	32.9	11.9	38.7, 39.6	18.0	23.2	6.1
12 "	13.7	43.9	29.1	43.4, 43.8	23.5	34.9	13.3
26 "	24.3, 23.8	44.5, 43.9	35.6	48.6, 48.2	39.4	43.9	19.7
50 "	32.7	45.2	40.5	.....	40.9	45.5	35.6
100 "	43.1	45.5	45.8	.....	46.0, 46.5	45.0	42.6
200 "	44.4, 45.2	45.7	46.6, 46.0	.....	45.0, 46.0	45.7	44.7, 44.8
					Acetylating Temperature 80°C.		
9 "	4.0	17.1	.....	17.3	.....	.....	.....
26 "	.....	39.0	13.9	41.6	.....	.....	.....
50 "	10.7	42.2	21.2	43.3	.....	.....	.....
100 "	11.2	45.4	34.0	46.6	.....	.....	.....
200 "	17.6	46.1	42.5	52.2	.....	.....	.....

TABLE VIII.

YIELD FROM FIVE GRAMS OF DRY STARCH

Time	Without Catalyst	Copper Sulfate	Trichloracetic Acid	Methylamine Sulfate	Acid Potassium Sulfate	Ferrous Sulfate	Disodium Phosphate
					Acetylating Temperature 100°C.		
2 hrs.	.....	.....	5.0	.....	5.3	.....	5.0
5 "	5.3	6.4	5.4	7.1	5.4	6.0	5.3
12 "	5.4	7.2	6.4	6.2	6.0	7.3	5.6
26 "	7.0	7.2	7.0	3.8	7.1	7.6	6.0
50 "	7.4	7.5	7.8	.....	8.0	7.7	7.5
100 "	7.9	6.3[1]	8.3	.....	6.3[1]	7.6	8.5
200 "	8.0	7.8	7.8	.....	8.2	7.8	8.6
					Acetylating Temperature 80°C.		
9 "	5.0	5.4	5.9	5.4	.....	.....	.....
26 "	5.0	7.2	5.5	7.8	.....	.....	.....
50 "	5.2	8.1	5.7	7.7	.....	.....	.....
100 "	5.4	7.6	7.5	7.0	.....	.....	.....
200 "	5.7	7.7	8.4	6.2	.....	.....	.....

1. Theoretical yield for a hexacetate on $C_{12}H_{20}O_{10}$ formula = 8.8 gms.

TABLE IX.

ACETYLATION OF CELLULOSE

PERCENTAGE OF ACETYL

Time	Without Catalyst	Copper Sulfate	Trichloracetic Acid	Methylamine Sulfate	Acid Potassium Sulfate	Stannous Chloride	Ammonium Persulphate
					Acetylating Temperature 80°C.		
9 hrs.	10.0	46.9, 46.7	14.2, 16.0	46.6	14.5	36.5	44.5
26 "	24.7	46.5, 47.2	27.0, 27.0	48.9, 49.5	38.2	41.0	46.6
50 "	46.5	47.3, 47.1	43.5	49.1	39.6	44.2, 45.8	46.6
100 "	46.3	46.8	47.1, 46.9	57.7, 56.9	44.6, 44.8	45.4, 45.6	55.5
200 "	46.7	47.0, 47.1	46.7	66.8[1]	46.3, 45.3	45.7, 45.4	55.4
300 "	.....	.....	.....	65.8[1]	.....	.....	.....
					Acetylating Temperature 60°C.		
1 "	.....	12.2	.....	.....	.....	.....	.....
2 "	.....	28.2	.....	.....	.....	.....	.....
4 "	.....	.....	.....	10.3	.....	.....	.....
8 "	.....	43.8	.....	35.0	.....	.....	.....
10 "	.....	.....	.....	44.1	.....	.....	.....
26 "	.....	45.5	.....	45.2	.....	.....	.....
50 "	.....	45.3	.....	45.2	.....	.....	42.3
100 "	.....	45.7	.....	46.1	.....	.....	46.5
200 "	44.5	.....	.....	.....	45.3	.....	.....

TABLE X.

YIELD FROM FIVE GRAMS OF DRY CELLULOSE

Time	Without Catalyst	Copper Sulfate	Trichloracetic Acid	Methylamine Sulfate	Acid Potassium Sulfate	Stannous Chloride	Ammonium Persulphate	Pyridin Sulfate
					Acetylating Temperature 80°C.			
9 hrs.	5.2	8.9	5.8	8.9	5.8	7.5	8.4	8.0
26 "	6.2	8.7	6.8	8.8	8.7	8.1	8.2	11.5
50 "	8.7	8.9	8.8	8.8	8.9	9.0	8.2	16.9
100 "	8.8	8.8	8.8	8.0	9.0	8.9	7.7	20.0
200 "	8.7	8.9	8.9	7.7	9.0	8.6	6.8	27.0
300 "	.....	.....	.....	6.9	.....	.....	.....	.....

Recent Investigations. According to E. Knoevenagel [1] acetylcelluloses are now made exclusively by the action of acetic anhydride on cellulose in presence of a catalyst, the use of acetyl chloride having been abandoned. Many catalysts, especially sulfuric acid, induce acetolysis of the cellulose molecule, a process quite distinct from hydrolysis and leading ultimately to the transformation of the cellulose into cellobiose octa-acetate and dextrose penta-acetate (see J.S.C.I., 1914, 102). Earlier methods of preparing acetone-soluble acetylcelluloses proved unsatisfactory because they involved decomposition of the cellulose molecule by hydrolysis or saponification and hence yielded products which gave solutions of low viscosity. A series of investigations in the author's laboratory has shown that by heating acetylcelluloses insoluble in acetone with ethyl acetate, benzene, acetone. alcohol, amyl alcohol, acetic acid, ethylene bromide, acetylene tetrachloride, cyclohexanone, etc., easily soluble acetylcelluloses can be obtained without any appreciable hydrolysis or saponification of the cellulose molecule. The transformation is accelerated by a small quantity of water and by neutral and acid salts, e. g., sodium ethylsulfate, methylamine bisulfate, zinc chloride, ammonium nitrate, aniline salts. The soluble acetylcelluloses prepared in this way are stated to possess more valuable qualities than those obtained by other methods. The

1. Zts. ang. Chem., 1914, **27**, 505; abst. J.S.C.I., 1915, **34**, 134; C.A. 1915, **9**, 524. Knoevenagel and v. Martius have shown that actone-insoluble cellulose acetates on heating at 100° in the complete absence of water and without a catalyst, but with ethyl acetate, benzene, acetone, ethyl alcohol, amyl alcohol, acetylene tetrachloride or bromide, or cyclohexanone, are transformed into easily soluble acetylcelluloses. Knoevenagel and H. Dieterich observed that these processes can be accelerated by using an appropriate catalyst, that strong saponifying actions must be avoided to secure the above reactions by more or less strong heating of the acetylcellulose. Neutral or acid salts have proved suitable as transformation accelerators, but so far no solvent alone acts as an accelerator.

For the manufacture of acetic anhydride, see R. Mueller and Deutsche Zelluloid Fabrik, D.R. Anm. M-54638, 1913; abst. Kunst. 1915, **5**, 36. Bosnische Elektrizitaets-Akt., D.R. Anm. B-75609; abst. Kunst. 1915, **5**, 36. General Chemical Co., D.R.P. 283163, 1910; abst. Kunst. 1915, **5**, 60. Naamlooze Vennootschap Fabriek van Chemische Produkten, E.P. 12042, 12130, 1913. For the preparation of acetic acid, compare Farbwerke vorm. Meister Lucius & Bruenig, D.R. Anm. F-36394, F-37851, 1913; abst. Kunst. 1915, **5**, 36. Akt.-Ges. f. Anilinfabrikation, D.R.P. 282263, 1914; abst. Kunst. 1915, **5**, 36. G. Calvert, E.P. 10687, 1913.

changes are attributed to intramolecular transformation of the cellulose acetate.

J. Hardcastle and A. Taylor [1] recommend as a varnish for woven fabrics such as are used in the manufacture of aeroplanes, balloons and similar air-craft, a combination of cellulose acetate, 1 to 2 parts; acetone, 8; alcohol, 3; benzene, 3; chloroform, 1, and trichlorethylene, 4 parts, the varnish being rendered more flexible, if desired, by the addition of 0.5 part of resorcinol diacetate. M. Bouffort [2] suggests that those portions of aviation and aeronautical apparatus which are usually opaque should, where possible, be constructed of a transparent composition having a cellulose acetate basis, in order to enlarge the field of vision and render the machine less visible. As a useful addition to acetate lacquers, coumarone and similar resins have been patented.[3]

C. Shrager and R. Lance [4] have described products consisting of mixtures of one or more metallic resinates, insoluble in water, and one or more glyceryl esters, which, when incorporated with a cellulose ester, give a plastic composition the properties of which can be varied according to the proportions and nature of the resinates employed. Example: 170 gms. of rosin are dissolved in 500 c.c. of benzene and the solution is

1. E.P. 13100, 1914; abst. J.S.C.I., 1915, **34**, 146.

2. F.P. 470897, 1913; abst. J.S.C.I. 1915, **34**, 173. For the manufacture of artificial sponge from nitrocellulose, acetylcellulose and viscose, see P. Raabe, Swiss P. 67258, abst. Kunst. 1915, **5**, 56. For the preparation of lacquers and films of combinations of nitrocellulose and acetylcellulose, consult the patented process of H. Dreyfus, D.R. Anm. D-30304, 1914; abst. Kunst. 1915, **5**, 36. The Zapon Lack-Ges. in their D.R.P. 281265; abst. Kunst. 1915, **5**, 33, describe cellulose acetate lacquers containing cumarone resin and other polymerization products of coumarone.

3. F. Lehmann, F.P. 469925, 471104, 1914; abst. J.S.C.I., 1915, **34**, 25, 187. For lacquers from para-coumarone and para-indene, refer to R. Lender, D.R.P. 277605, 1913; abst. J.S.C.I., 1915, **34**, 187. M. Wendriner, D.R.P. 270993, 281432, 1913; abst. Kunst. 1915, **5**, 33. See also F. Lehmann, F.P. 468082; abst. Kunst. 1915, **5**, 56.

4. F.P. 470726, 1913; abst. J.S.C.I., 1915, **34**, 173. The cement patented by A. Tessler (U.S.P. 1122554, 1914; abst. C.A. 1915, **9**, 516) for joining portions of moving picture films, comprises celluloid 1, acetylcellulose 3, acetone 47, chloroform 21.5, glacial acetic acid 21.5, and amyl acetate or other high boiling volatility decreaser, 6 parts. For non-inflammable cinematographic film substances, see Comp. Gen. des Etabl. Pathe Freres, E.P. 2067, 1915; F. Appl. Feb. 11, 1914; abst. J.S.C.I., 1915, **34**, 14.

shaken for several hours with 17 gms. of zinc oxide and 3 of aluminum oxide. To the solution of mixed resinates, 30 gms. of triacetin is added and the solvent evaporated. A mixture of equal parts of the plastic product and nitrocellulose possesses properties analogous to those of camphor celluloid.

The Verein f. Chem. Ind. in Mainz [1] have described cellulose acetates characterized by their infusibility and the exceptional viscosity of their solutions prepared by the acetylation of perfectly anhydrous cellulose: 30 kilos of cotton is digested in a mixture of 60 kilos of acetic anhydride and 100 of glacial acetic acid at 50°-100° for several hours or at the ordinary temperature for a few days; when the moisture is completely eliminated, a catalytic agent is added, preferably dissolved in a further quantity of acetylating mixture, and acetylation is performed in the usual manner.

In the preparation of cellulose esters and acetates suitable for film and other manufacture, the Fabriek van Chemischen Produkten [2] take air-dry cotton, 106 gms., which is treated with a mixture containing approximately 240 gms. of acetic anhydride, 400 of acetic acid and 15 of acetylsulfuric acid (see F.P. 461,539; J.S.C.I., 1914, 219). When the com-

1. F.P. 470963, 1914; abst. J.S.C.I. 1915, 34, 173. For an improvement claimed in the manufacture of artificial filaments by means of gelatin, formaldehyde collodion, cellulose acetate and viscose, consult H. Davoine, F.P. 470606; abst. Kunst. 1915, 5, 56. H. Dreyfus (Swiss P. 67113; abst Kunst. 1915, 5, 57) alleges a process for increasing the solubility of cellulose acetates, based upon the observation that those esters readily or difficulty soluble in chloroform may be transformed into modifications dissolving in acetone with facility, by treatment of the ester in solution with dilute organic or inorganic salts.

2. F.P. 470384, 1914; abst. J.S.C.I., 1915, 34, 172. In the Knoll & Co. E.P. 2491, 4353, 1913; abst. Kunst. 1914, 4, 377, process for acetylcellulose formation, 1 part of cellulose is treated with 4 parts glacial acetic acid and 0.02 parts recently sublimed ferric chloride and 5 parts acetic acid anhydride at a temperature of 70° until the cellulose passes into solution in the reacting mixture). 8% water is then added and hydrolysis continued to the point of desired solubility. Instead of anhydrous ferric chloride, zinc chloride, ammonium chloride, cupric chloride, ammonium nitrate and stannous chloride are claimed as equally efficient. Compare in this connection D.R. Anm. C-24886, 1914; abst. Kunst. 1915, 5, 36. The Kgl. Materialpruefungsamt (Kunst. 1915, 5, 36) in tests of the relative efficiency of cellon films, of 0.75 mm. thickness, obtained the following results: Firmness, 286.6 kilos per square ccm. Extension, 55%. Breaking strain, 2125 meters.

bined acetic acid amounts to 56-62% of the dry weight of the product, the mixture is treated with 40 c.c. of 10% aqueous sulfuric acid and any sulfuric acid remaining in combination with the ester is eliminated by digesting at 40° C. for tion with the ester is eliminated by digesting at 40° for lose *tri-* and *di-*acetates, giving viscous solutions with acetone and capable of withstanding 200° without decomposition.

In the preparation of plastic masses containing acetylcellulose as worked out by A. Eichengruen,[1] the cellulose ester is kneaded with small amounts of camphor substitutes such as dichlorhydrin, manol (acetyl methylaniline), or naphthyl acetate, and small amounts of liquid solvents which are solvents of the above bodies but non-solvents of acetylcellulose, or if acetylcellulose solvents be used they are employed in insufficient quantities for solution, and only sufficient for incipient gelatinization and colloiding.

1. E.P. 27258, 1910. Accordng to Swiss P. 61930; abst. Kunst. 1914, 4, 378, L. Lederer prepares technically useful acetylcelluloses by means of the usual mixtures of acetic acid, acetic anhydride and sulfuric acid, but subsequently hydrolyzes by the use of aqueous sodium acetate. Knoll & Co., Aust. P. 64085, abst. Kunst. 1914, 4, 377, convert difficultly soluble cellulose acetate into more soluble modifications by treatment with benzene, a little sulfacetic acid with acetic anhydride, until the solubility in chloroform entirely disappears.

ERRATA.

Page		Line	From	For	Read
2501	Notes	1 and 2	Bottom	Part	Volume
2525	Notes	21	Top	Bennesch	Benesch
2533	Text	4	Top	Erwigs	Erwig
2615	Text	9	Top	Fisher	E. Fischer
2629	Notes	5	Bottom	9357	9537
2630	Notes	9	Bottom	276262	376262
2632	Notes	4	Bottom	267577	267557
2666	Notes	2	Top	433264	432264
2668	Notes	8	Top	4145	4154
2669	Notes	15	Top	12278, 1906	12278, 1905
2683	Notes	12	Bottom	872	8072
2683	Notes	11	Bottom	74	741
2686	Notes	11	Bottom	1900	1910
2752	Notes	2	Top	Note 6	1
2752	Notes	3	Bottom	Omit entire line	
2756	Notes	1	Top	14217	15217
2757	Notes	2	Top	Elaktrochem	Elektrochem
2768	Text	2	Bottom	Omit entire line	
2773	Notes			Transpose last two lines	
2841	Notes	5	Top	233876	233786
2901	Text	11	Top	chlorofor mand	chloroform and
2907	Notes	16	Bottom	10377, 1914	10377, 1913
2907	Notes	15	Bottom	ovide	oxide
2907	Notes	14	Bottom	Atrospheres	Atmospheres
2910	Text	9	Top	aceti cacid	acetic acid
2910	Text	6	Bottom	otal	total
2912	Text	5	Top	$100%	100%
2932	Note	2	Add	Zts. ang. Chem.	1906, 993

INDEX OF PATENTS

Compiled by

JOHN W. BRUCE, F. C. S.

NOTE.—In the United States Patents, the Patent Applications are given first, then the Reissue of Patents, and lastly the Issued Patents. The English (British) Patents follow numerically under the respective years of issue. In indexing the French Patents, where there is one or more addition patents, the word "addition" is stated on a line separate from the pagination of the French Patent, the Addition Patents being given separately after the French Patents, either by date or wherever possible, by the addition number. The German Patent Applications are first recorded, alphabetically under the respective application classes, followed by the issued Patents, numerically arranged. It has been impossible to determine, in some instances, whether certain Austrian inventions have been issued under the Patent Application or Patent issuance number. Hence both have been incorporated in one table, arranged numerically but with the addition of the year of issuance, where possible to obtain and verify. The entire work will close with complete collective indices of all the separate volumes, comprising about two hundred thousand separate citations.

UNITED STATES

APPLICATIONS

24575, 2553, 2554
637857, 2584
637858, 2584

RE-ISSUES

11997, 685127, 2633, 2637, 2639, 2640, 2641, 2658, 2668, 2695, 2847
12637, 2539, 2567, 2569, 2675

PATENTS

126698, 2887
366231, 2710
410205, 2710
410206, 2710
417202, 2865
420445, 2568
420446, 2554
420447, 2568
429445, 2554
458663, 2865
503402, 2666
517987, 2709
528812, 2709, 2710
530826, 2556, 2721, 2888, 2928
532468, 2525, 2845
543197, 2712
542692, 2715
543198, 2715
551456, 2709
552209, 2715
552934, 2715
553270, 2715
564343, 2715
566349, 2715
568106, 2715
572135, 2669, 2715
573928, 2865
583516, 2715
587097, 2814
596662, 2707
598649, 2709
599631, 2865
607554, 2715
610861, 2865
619617, 2865
627031, 2558, 2663, 2736, 2738
627493, 2814
632605, 2557, 2634, 2639, 2640, 2736, 2738
649852, 2846
650431, 2880
654988, 2558, 2775, 2929
667600, 2880
679203, 2526, 2559
679204, 2664
689536, 2880
690211, 2631, 2681, 2696, 2860
692497, 2559, 2664, 2928
694946, 2803
695127, 2633, 2637, 2639, 2640, 2641, 2658, 2668, 2695, 2847
700884, 2710
707306, 2804
708456, 2562, 2928
708457, 2562
709922, 2590, 2819, 2930

710648, 2527
712200, 2668, 2669, 2681, 2697, 2819
714484, 2521
726614, 2866
729990, 2630, 2651, 2696, 2760, 2765, 2860
733729, 2657, 2929
734123, 2560, 2562, 2630, 2663, 2670, 2675, 2686, 2687, 2702, 2721, 2727, 2738, 2754, 2775, 2776, 2858
735948, 2723, 2866
738533, 2696, 2703, 2775
752388, 2858
753206, 2886
753300, 2886
758335, 2714
768073, 2857
774677, 2630, 2668, 2679, 2697, 2698, 2763
774713, 2559, 2667, 2668, 2700, 2761
774714, 2667, 2668, 2700, 2761
776192, 2639
776480, 2639
778173, 2520, 2525, 2641, 2680, 2893
779553, 2639
789249, 2814
790565, 2561, 2562, 2630, 2663, 2670, 2675, 2686, 2687, 2702, 2721, 2727, 2738, 2754, 2776, 2777, 2826, 2858
792001, 2851
792149, 2681, 2695, 2819
794581, 2688, 2793
794789, 2723
794970, 2723
804516, 2740
804960, 2628, 2745, 2764, 2796
806660, 2516
808100, 2723
809935, 2562, 2663
812098, 2563, 2670, 2758
826229, 2593, 2931
826781, 2802
830493, 2772
831028, 2707
831488, 2708
831725, 2742
835307, 2723
838350, 2539, 2567, 2569, 2675, 2826
845322, 2724
848357, 2814
854374, 2605, 2758
855556, 2630, 2676, 2681, 2880
857046, 2517
857960, 2886
864123, 2866
870518, 2723
875232, 2723
880900, 2722
884475, 2639, 2801
888516, 2687, 2695, 2824, 2828
891218, 2603, 2636, 2698
891753, 2519
892899, 2706, 2710
894148, 2728
900204, 2669, 2715
902093, 2613, 2724, 2758
904269, 2687, 2695, 2824, 2828
908051, 2742
909288, 2814
910920, 2728
919759, 2891
920828, 2843
922340, 2519, 2631, 2680, 2681, 2821
924304, 2725
931629, 2888
933107, 2677
939350, 2871
941159, 2896
944372, 2521
951582, 2887
952724, 2668, 2672, 2694, 2698, 2700, 2766
953175, 2866
953454, 2681, 2880
953677, 2620, 2621, 2624
954310, 2555
955082, 2620, 2621, 2624
960927, 2516
961241, 2699, 2837, 2838
961360, 2629, 2691, 2708
962877, 2630, 2681, 2687, 2688, 2695, 2696, 2711, 2880
970145, 2518
970825, 2518
970972, 2871
972464, 2629, 2693
975151, 2518
975866, 2518
976594, 2803
976994, 2802
979966, 2699, 2837, 2839
981574, 2699, 2837
984805, 2802
985528, 2743
987692, 2595, 2676
988965, 2664, 2727, 2863
991205, 2757
992551, 2722
994738, 2621, 2628, 2841
992743, 2802
996191, 2711
998995, 2724, 2750
999236, 2605, 2636, 2640, 2723
999490, 2633, 2641, 2658, 2673, 2679, 2688, 2696, 2766
999491, 2725
999955, 2692, 2694
1000040, 2692, 2694
1002408, 2699, 2837
1003438, 2630
1005454, 2630, 2666, 2679, 2698, 2761
1008333, 2666
1008438, 2718
1008489, 2565
1008557, 2565
1009116, 2629, 2665, 2746, 2862
1009428, 2723
1010222, 2815
1010797, 2724
1010869, 2724
1011443, 2802
1014859, 2694
1015155, 2630, 2664, 2688, 2690, 2736, 2758,
1015156, 2664, 2695, 2699, 2736, 2739, 2780, 2783
1017023, 2504
1017261, 2517, 2519
1019230, 2519
1025731, 2639, 2676, 2732, 2804
1027486, 2631, 2737
1027614, 2630, 2737
1027615, 2631, 2737
1027616, 2631, 2737
1027617, 2630, 2737
1027618, 2631, 2737
1027619, 2629, 2697
1028748, 2648, 2649, 2724

1029341, 2632, 2681, 2696
1030311, 2606
1030916, 2743
1031616, 2685, 2686, 2689, 2691, 2694, 2695, 2696, 2697, 2698, 2699, 2700, 2702, 2736, 2823, 2825
1033841, 2694
1035108, 2746, 2796, 2862
1036224, 2741, 2751
1036461, 2724
1038783, 2724
1038900, 2750
1039782, 2693
1040323, 2735
1041112, 2753
1041113, 2703, 2767
1041114, 2739
1041115, 2684
1041116, 2761
1041117, 2701
1041118, 2701, 2761
1041587, 2842
1043985, 2518
1045139, 2742
1045895, 2669, 2716, 2797
1045990, 2608, 2683, 2697
1046729, 2620, 2627, 2687
1050065, 2608, 2683, 2697
1051165, 2602, 2621
1055513, 2627
1061771, 2584, 2611, 2861
1061977, 2620
1066474, 2717
1067785, 2608, 2683, 2697
1069168, 2527
1069445, 2595
1074092, 2584
1074633, 2593, 2900
1075284, 2717
1076215, 2770
1076216, 2770
1079733, 2903
1079778, 2667, 2732, 2795
1081959, 2522
1082167, 2596
1082424, 2717
1083589, 2519
1084581, 2685, 2932
1089482, 2886
1089910, 2689, 2691
1090074, 2594, 2598
1090440, 2747
1090730, 2809
1093247, 2621
1095099, 2752
1104978, 2907
1105619, 2772
1107222, 2862
1109512, 2903
1112890, 2901
1113927, 2909
1122554, 2900, 2956
1128468, 2932

ENGLISH

1878

2484, 2801

1890

20973, 2568

1891

22610, 2801

1892

4169, 2801
7688, 2801

1893

4214, 2866

1894

9676, 2534, 2556, 2721
21331, 2709

1896

6711, 2523

1897

12952, 2523
26381, 2857

1898

3770, 2857
18283, 2558, 2663, 2736, 2738
22029, 2557, 2634, 2639, 2640, 2736, 2738
24662, 2639, 2641, 2658, 2846

1899

63, 2857
5793, 2866, 2896
13287, 2712
14233, 2670
14525, 2866
22867, 2880
25297, 2523
25434, 2714
25735, 2692

1900

9088, 2857
11749, 2558, 2559, 2687, 2723
11751, 2712
13131, 2714
17687, 2891
17948, 2710, 2713
19039, 2526, 2559, 2664
20723, 2712

1901

3392, 2523
4326, 2712
5404, 2890
6246, 2802
8072, 2682, 2683
10213, 2715
12863, 2701, 2705
13733, 2723
20747, 2857
21268, 2858
21628 2560, 2562, 2630, 2663, 2670, 2675, 2686, 2687, 2702, 2721, 2727, 2754, 2776, 2820, 2826, 2841, 2903
22181, 2890
22662, 2705, 2711
23892, 2809
25688, 2723
26075, 2696, 2708, 2764, 2775

1902

2264, 2637, 2639, 2640, 2641, 2658, 2668, 2695, 2847
3923, 2521
4383, 2683
4886, 2566
5348, 2804
7068, 2630, 2668, 2679, 2697, 2698
9304, 2814
9868, 2520, 2525, 2641, 2690, 2893
10872, 2520, 2525, 2643
11164, 2555, 2901, 2929

11997, 2851
14032, 2527
16102, 2903
17311, 2802
19437, 2866
19565, 2851
19872, 2680
20660, 2590, 2819
22096, 2521
23445, 2682
25243, 2866
25821, 2858
28595, 2523

1903

4863, 2650, 2676, 2761
7341, 2663, 2667, 2758, 2820
7346, 2562, 2664
10243, 2601, 2602, 2667, 2721
14483, 2688, 2695, 2805, 2824, 2828
15490, 2880
17156, 2750
17430, 2903
25390, 2859

1904

3855, 2858
7534, 2516
13983, 2724
15435, 2705
16756, 2757
18602, 2740, 2741, 2743
19066, 2903
19568, 2740
24083, 2563, 2670, 2758
28733, 2775, 2820

1905

2817, 2705
2880, 2881
6751, 2628, 2745, 2764, 2796
9404, 2723
9998, 2548, 2593, 2931
11512, 2707
12277, 2630, 2665, 2666, 2668, 2669, 2700, 2766, 2861
12278, 2630, 2665, 2666, 2668, 2669, 2700, 2766, 2861
19330, 2567, 2607, 2675
21518, 2757
22094, 2742

1906

1939, 2836
2156, 2854
2817, 2705
4597, 2687, 2695, 2805, 2824, 2828
8077, 2674, 2677, 2701, 2706
10228, 2706, 2713
10228A, 2701, 2706, 2710
12718, 2502
14255, 2601, 2636, 2721, 2747
14438, 2517
16271, 2705, 2715
19107, 2648, 2649, 2724
20037, 2698, 2708, 2716
22038, 2518
23688, 2829
23780, 2729
24067, 2572, 2576, 2675, 2682, 2727, 2736, 2738, 2753, 2826
26501, 2613, 2724, 2758
26502. 2593, 2697, 2805, 2822
26503, 2525, 2667, 2859

1907

592, 2687, 2695, 2824, 2828
2026, 2594, 2820
2026A, 2597, 2635
2026B, 2603, 2636, 2698
2461, 2859
2511, 2525, 2620, 2621, 2630, 2680, 2681
3103, 2605, 2636, 2640 2723
5016, 2843
8369, 2592
9537, 2629, 2672, 2686, 2710, 2745, 2760
13023, 2708
13411, 2742
13508, 2674
19576, 2725
20125, 2522
24284, 2699, 2837
25274, 2896
26915, 2891
28743, 2814

1908

741, 2724
3428, 2517
3849, 2579
8727, 2592
19735, 2630, 2663, 2676, 2686, 2687, 2689, 2721, 2768
21280, 2750
25433, 2526
27201, 2762

1909

3704, 2724
4154, 2668, 2672, 2694, 2699, 2700, 2766
6554, 2631, 2681
7743, 2699, 2837
8945, 2671, 2692, 2763
10578, 2805
11354, 2630, 2685, 2686, 2689, 2691, 2694, 2695, 2696, 2697, 2698, 2699, 2700, 2901, 2702, 2736, 2823
11625, 2651, 2676, 2747, 2842, 2861
12976, 2630, 2765, 2784, 2860
14407, 2863
15855, 2710
16199, 2813
17036, 2620, 2621, 2624
17449, 2806
18028, 2521
18193, 2630, 2685, 2686, 2689, 2691, 2694, 2695, 2696, 2698, 2699, 2700, 2701, 2702, 2736, 2823, 2825, 2826
20893, 2517
20965, 2898
22085, 2793
24299, 2703
24556, 2871, 2898
26657, 2581, 2607, 2630, 2666, 2667, 2672
27102, 2586
28293, 2903

1910

476, 2630, 2666, 2679, 2698, 2761, 2901
555, 2902
636, 2809
870, 2805
951, 2900

1441, 2664, 2695, 2699, 2736, 2739, 2780, 2783
3096, 2631
3559, 2864
3603, 2863
3606, 2867
4684, 2906
4959, 2811
4976, 2909
5939, 2909
6608, 2684
8438, 2516
8646, 2640, 2684, 2695, 2696
8647, 2640, 2684, 2695, 2696
10794, 2608, 2629, 2683, 2697
10795, 2608, 2629, 2683, 2697
12233, 2724
12406, 2639, 2676, 2732, 2804
12422, 2685
13100, 2630, 2685, 2686, 2689, 2691, 2694, 2695, 2696, 2698, 2699, 2700, 2701, 2702, 2736, 2823, 2827
13692, 2629, 2692, 2708
14194, 2881
14271, 2595, 2676
14293, 2665, 2670, 2688, 2796, 2805
14364, 2664, 2676, 2721, 2753, 2762
15288, 2743, 2750
15700, 2620, 2627
16932, 2664, 2727, 2762
18076, 2664, 2695, 2699, 2736, 2739, 2780, 2783
18189, 2768
19679, 2909
20672, 2584, 2611, 2822, 2840
21719, 2879
23573, 2903
23923, 2909
23924, 2527
24382, 2602, 2621, 2626
24980, 2626
25274, 2902
25967, 2742
26334, 2902
26928, 2901
27250, 2630, 2668, 2669, 2673, 2701, 2736, 2740
27258, 2958
28839, 2523
28848, 2608
29246, 2621, 2631, 2687
29273, 2899

1911

309, 2631, 2687
611, 2526
1556, 2621, 2628, 2841
2375, 2743
3139, 2685, 2693
3384, 2898
3973, 2520, 2525, 2633, 2821
4099, 2666
4744, 2667, 2732, 2735
6241, 2620, 2627
6798, 2884
7442, 2811
8313, 2631, 2632, 2681, 2696
11728, 2630, 2639, 2718
12207, 2909
14142, 2681
14433, 2898
15204, 2674
16000, 2565
16295, 2674
17259, 2666, 2712
17424, 2521
20975, 2583, 2768
20976, 2583, 2695, 2697 2701, 2753
20977, 2607, 2676
20978, 2607, 2629, 2664, 2676
20979, 2607
21426, 2884
22237, 2565, 2621, 2625, 2640, 2658
23995, 2718
25449, 2901
25570, 2909
25805, 2901
25893, 2903
26036, 2735
26997, 2898
27491, 2897
28609, 2909

1912

304, 2909
613, 2900
784, 2518
822, 2565
1105, 2741, 2751
1598, 2672
2527, 2641
2859, 2565
3869, 2595, 2669, 2716, 2797
4044, 2898
6798, 2702, 2883
7259, 2722
7292, 2669, 2797
7687, 2578, 2605
8076, 2521, 2522
8990, 2578, 2590
10706, 2597, 2652, 2835
12230, 2898
12854, 2505
12995, 2842
13239, 2689
14537, 2899
15868, 2596
16133, 2608
16620, 2727
17574, 2902
18822, 2767, 2904
20527, 2575, 2588, 2702
20852, 2583, 2607, 2664, 2676
21376, 2583, 2607, 2664, 2676
22645, 2607
23728, 2566, 2770
23777, 2900
24327, 2521
25893, 2606
26987, 2889
27227, 2582, 2595
27228, 2595
28210, 2809

1913

1156, 2577
1315, 2882
2178, 2595, 2596
2425, 2890
2491, 2581, 2595, 2900, 2957
3261, 2909
3849, 2578, 2580
3991, 2900
4353, 2581, 2900, 2957
5810, 2909
6035, 2505
6387, 2508, 2593
7038, 2855

7418, 2813
8676, 2586
10377, 2907
10687, 2521, 2907, 2955
12042, 2907, 2912, 2955
12130, 2907, 2955
13882, 2593, 2900
14246, 2932
15762, 2900
15880, 2899
16849, 2909
26905, 2581, 2769, 2900
16940, 2578
17016, 2522
18105, 2771
18499, 2904
19008, 2903
19016, 2909
19017, 2909
19018, 2909
21015, 2811
22826, 2842
29882, 2576

1914

1156, 2597, 2625, 2652, 2835
5633, 2884
7899, 2813
9266, 2578
13100, 2956
13696, 2606
14042, 2564, 2596
15544, 2824
21016, 2762
21524, 2834
22718, 2903

1915

75, 2903
2067, 2956

FRENCH

Feb. 11, 1914, 2956
280248, 2549, 2558
282320, 2558, 2663, 2736, 2738
292983, 2712
296132, 2891
300672, 2716
301703, 2712
301749, 2558, 2929
304723, 2526, 2559, 2664
305481, 2712
308372, 2712
308506, 2560, 2664
309759, 2559
309962, 2682
309963, 2712
310942, 2716
312046, 2723
312086, 2716
312817, 2701, 2705
312846, 2705
315938, 2526, 2527
316060, 2677
316061, 2677
316229, 2809
316500, 2566
317007, 2560, 2630, 2663, 2670, 2676, 2686, 2687, 2702, 2721, 2727, 2738, 2754, 2776, 2820, 2826, 2858, 2901
317008, 2696, 2703, 2775
317607, 2705
318710, 2521
319648, 2603
319724, 2559, 2630, 2668, 2679, 2697, 2698
319848, 2559, 2687, 2734, 2929, 2931
320027, 2716
320269, 2723
320885, 2555
321803, 2857
322206, 2520, 2525, 2648, 2680
322506, 2707
324121, 2650, 2676, 2761
324718, 2664, 2761, 2856
324862, 2590, 2819
326468, 2858
327322, 2723
327969, 2722
329117, 2886
330714, 2663, 2667, 2758, 2763, 2820
331819, 2716
334154, 2520, 2525, 2680, 2893
338849, 2694, 2707, 2881
338965, 2522
339134, 2725
340266, 2710
341007, 2667, 2787
341556, 2705, 2709
341764, 2516
342168, 2516
345764, 2593
346562, 2741
347906, 2564, 2670, 2758
349970. 2707
350313, 2758
350442, 2820
352853, 2710
352896, 2764
352897, 2628, 2745, 2764, 2796
354942, 2630, 2665, 2666, 2667, 2679, 2700, 2766, 2861
355423, 2723
355776, 2741
357432, 2521
357473, 2858
357781, 2723
358079, 2554, 2567, 2675
358146, 2742
360180, 2522
360249, 2522
361379, 2675, 2677
361394, 2801
362721, 2836
363090, 2698, 2709, 2713
363846, 2706, 2710
364604, 2708
365297, 2710
366106, 2701, 2706, 2710, 2724
367316, 2517
368738, 2601, 2636, 2721, 2747
368766, 2648, 2649, 2724
369123, 2594, 2598, 2820
370224, 2735
370249, 2735
371356, 2605, 2613, 2724, 2758
371357, 2593, 2697, 2822, 2930
371358, 2525, 2667, 2859
371447, 2572, 2576, 2675, 2682, 2727, 2736, 2738, 2754, 2826
372512, 2710
372714, 2518
373854, 2692
373994, 2603, 2698
374370, 2605, 2636, 2640, 2723
374395, 2711
375092, 2639, 2641, 2658, 2686, 2687, 2853
375167, 2728
376262, 2525, 2620, 2621, 2630, 2680, 2681

376269, 2708
376578, 2592, 2930
376578, Addition.
377010, 2629, 2672, 2686, 2710, 2745, 2760
377671, 2705
378713, 2742
381430, 2725
382270, 2710
382339, 2517
382350, 2711
383064, 2843
383636, 2695, 2837, 2838
383705, 2729
383902, 2896
384079, 2703
384111, 2866
384112, 2866
385179, 2601, 2637, 2639, 2667, 2695, 2697, 2724, 2737
385180, 2601, 2637, 2639, 2667, 2695, 2697, 2724, 2737
385900, 2814
386017, 2728
386734, 2520
387179, 2711
387537, 2711
388097, 2716
388755, 2866
389039, 2517, 2519
391785, 2866
392504, 2724
393526, 2518
393963, 2630, 2663, 2676, 2686, 2687, 2689, 2721
396467, 2810
397092, 2891
397429, 2630, 2686, 2689
398028, 2802
400652, 2520, 2631, 2680, 2681, 2821
401228, 2764, 2863, 2867
402028, 2668, 2672, 2694, 2699, 2700, 2766
402072, 2648, 2649, 2651, 2676, 2724, 2747, 2842, 2861
402083, 2671, 2692, 2860
402235, 2722
403761, 2806
404360, 2521
404886, 2710
405293, 2620, 2621, 2624
407046, 2526
407932, 2805
408370, 2630, 2685, 2686, 2689, 2691, 2694, 2695, 2696, 2698, 2699, 2700, 2701, 2702, 2736, 2823, 2825
408396, 2754
409065, 2586
409557, 2716
410721, 2811
410725, 2863, 2867
411126, 2630, 2765, 2784, 2860
411298, 2630, 2666, 2679, 2698, 2761
412503, 2864
412797, 2664, 2695, 2699, 2736, 2739, 2780, 2783
413657, 2640, 2684, 2695, 2696
413658, 2640, 2684, 2695, 2696
413671, 2586, 2822
413787, 2822
413901, 2811
414679, 2640, 2684, 2695, 2696
414680, 2640, 2684, 2695, 2696
415517, 2608, 2629, 2683, 2697
415518, 2629, 2683, 2697
416752, 2584, 2611, 2822, 2840
416843, 2692
417027, 2630, 2689, 2823
417250, 2664, 2676, 2721, 2753
417274, 2595, 2676
417319, 2629, 2665, 2746
417815, 2516, 2517
418309, 2664, 2727
418347, 2702, 2747, 2755, 2756, 2796, 2852
418518, 2608
418744, 2768
419530, 2630, 2668, 2669, 2673, 2746
420127, 2805
420197, 2870
420346, 2527
420489, 2743
420555, 2879
420856, 2620, 2627
421010, 2581, 2630, 2666, 2667, 2672
421227, 2516
421249, 2527
421843, 2766
421854, 2612, 2682, 2696
422542, 2621, 2626
423197, 2602, 2621, 2626
423774, 2621, 2631, 2687
424428, 2815
424621, 2621, 2631, 2687
425321, 2516, 2518
425327, 2743
425900, 2685, 2693
426436, 2520, 2525, 2635, 2821
427265, 2587, 2675, 2683, 2686
427425, 2628
427445, 2621, 2841
427562, 2747
427804, 2630, 2664, 2686, 2700
427818, 2882
428069, 2631, 2632, 2681, 2696
428315, 2724
428554, 2576
429754, 2630, 2718
429788, 2702, 2755, 2796, 2806, 2883
430606, 2595, 2621, 2626, 2637, 2639, 2723
432046, 2607, 2664, 2676
432047, 2630, 2695, 2697, 2701, 2732, 2753
432264, 2629, 2630, 2666, 2668, 2669, 2671, 2679, 2689, 2695, 2696, 2697, 2702, 2728, 2732, 2737, 2766, 2768
432747, 2565
432751, 2588
433309, 2742
435507, 2565, 2621, 2625, 2640, 2658
435742, 2685
436100, 2754
436538, 2769
436900, 2606
437240, 2606
437315, 2735
437411, 2762
437473, 2606
438649, 2577, 2699
438965, 2518

439732, 2674
440133, 2667, 2732, 2735
440658, 2522
440733, 2669, 2691, 2797
440955, 2690
441146, 2667
441249, 2751
441864, 2578
442512, 2578, 2771
442738, 2527
443018, 2724
443031, 2699
443897, 2504
444568, 2842
445638, 2882, 2885
445770, 2846
445798, 2652
445866, 2757
446263, 2727
446627, 2884
447645, 2679, 2767
447974, 2505
448072, 2575
448342, 2526, 2613
448364, 2674
449253, 2852, 2884
449605, 2712
449606, 2712, 2716
449607, 2712
449622, 2521
450746, 2748
450886, 2605, 2613
450890, 2579, 2595
450967, 2901
451374, 2674
452374, 2578, 2579, 2580, 2595, 2596
452432, 2685, 2761, 2765
453164, 2712
453395, 2731
453464, 2855
453835, 2578, 2581, 2595
454753, 2654
455117, 2578, 2579, 2583, 2903
455811, 2813
457925, 2814, 2863
458263, 2584, 2596
459282, 2593, 2900
460807, 2747
460971, 2522
461034, 2720
461058, 2625, 2811, 2885
461121, 2771
461450, 2527, 2912
461539, 2957
461544, 2691, 2768, 2899
462274, 2507, 2903
462711, 2729
463156, 2770
463498, 2835, 2903
463613, 2762, 2855
463616, 2762
463622, 2835, 2884
464617, 2800
465345, 2771, 2772
466009, 2582
468062, 2956
468983, 2906
469017, 2903
469371, 2903
469925, 2903, 2956
470384, 2957
470606, 2957
470726, 2956
470897, 2956
470963, 2957
471104, 2956

ADDITION PATENTS

280248, Oct. 19, 1898
2549, 2558
296132, 1st Add. 3962
2891
301703, Oct. 8, 1900
2712
308372, 1st Add.
2712
312046, 1st Add. Aug. 18, 1904
2723
317007, Add. 1425,
2562, 2663, 2664,
319724, Add. 811
2630, 2668, 2679, 2697, 2698
320027, 1st Add. Nov. 3, 1902
2716
2nd Add. Jan. 5, 1905
2716
338849, 1st Add.
2694, 2881
2nd Add.
2707, 2881
354942, 1st Add. June 8, 1905
2630, 2665, 2666, 2667, 2669, 2700
2766, 2961
361879, 1st Add. July 7, 1906
2675, 2677
2nd Add. Mch. 8, 1907
2677
3rd Add. Oct. 3, 1907
2677
363846, 1st Add. May 16, 1906
2706
374395, 1st Add. Apr. 13, 1907
2711
376578, Add. 9194
2592
383636, 1st Add. Apr. 5, 1909
2699, 2837
384111, 1st Add.
2866
2nd Add.
2866
3rd Add.
2866
4th Add. Aug. 31, 1907
2866
384112, July 6, 1907
2866
387537, 1st Add. May 8, 1908
2711
407046, 1st Add. Oct. 16, 1909
2526
2nd Add. Dec. 29, 1910
2526
408370, Add. 12469
2630, 2685, 2686, 2689, 2691, 2694, 2696, 2698, 2700, 2701, 2702, 2736, 2823, 2836
Add. June 11, 1910
2630, 2685, 2686, 2689, 2691, 2694, 2695, 2696, 2699, 2701, 2702, 2736, 2823, 2827

410725, Add. March 18, 1910 2863
412797, Add. 12388 2664, 2695, 2699, 2736, 2739, 2780, 2783
417274, Add. 18345 2595
418347, Add. 15217 2702, 2747, 2756, 2796, 2852
419530, Add. 13237 2630, 2668, 2669, 2673, 2746
420856, Add. March 13, 1911 2620, 2627
427818, Add. 14044 2882
432046, 1st Add. 14558 2607, 2676
2nd Add. 14559 2607, 2676
3rd Add. 15933 2607, 2676
4th Add. 15894 2607, 2676
5th Add. 15933 2607
6th Add. 16316 2607, 2676
7th Add. 16494 2607, 2676
8th Add. 15719 2695, 2697 2701
432264, 1st Add. Nov. 19, 1912 2629, 2666, 2668, 2669, 2671, 2679, 2689, 2695, 2696, 2697, 2702, 2737, 2766
2nd Add. July 15, 1911 2699
3rd Add. Sep. 13, 1911 2629
Add. 16854 2629
443018, Add. 16380 2724
448342, 1st Add. April 18, 1913 2526
Add, 17674 2613
452874, 1st Add. Jan. 16, 1913 2580
Add. 17104 2578, 2596

GERMAN

APPLICATIONS

June 28, 1913 2824
23476, 2801
25533, 2863
A 17838, 2527
A 21107, 2565
A 21632, 2527
A 28352, 2577
B 50757, 2869
B 63482, 2842
B 64397, 2797
B 68616, 2767
B 69304, 2627
B 71109, 2663
B 75609, 2955
C 12963, 2593
C 19868, 2821
C 21388, 2596
C 21994, 2580, 2596
C 22873, 2796
C 22897, 2686, 2693
C 23158, 2821, 2885
C 23487, 2821, 2885
C 23703, 2596
C 24886, 2957
D 23457, 2724
D 24553, 2843
D 27465, 2526
D 27952, 2526
D 29058, 2904
D 29439, 2607
D 29692, 2724
D 30304, 2956
E 1558, 2595
E 14210, 2813
E 14310, 2561
E 14630, 2813
E 14993, 2561
E 14998, 2561
E 15581, 2561
E 17505, 2561, 2800
E 20963, 2554, 2567
F 14998, 2595
F 27152, 2812
F 27686, 2812
F 28111, 2561, 2664 2676, 2721, 2753
F 28283, 2561
F 32823, 2561, 2595
F 36394, 2955
F 37851, 2955
H 57941, 2576
I 14379, 2663
J 14823, 2626
J 15495, 2626
K 36905, 2771
K 47775, 2578
K 48996, 2769
K 48490, 2581, 2769
K 50333, 2578, 2603
K 50334, 2603
K 50605, 2603
K 50960, 2603
K 52025, 2581, 2769
K 52789, 2581, 2769
L 15787, 2566
L 30181, 2701
L 30386, 2692, 2701
L 32835, 2884
M 28289, 2554, 2567, 2675
M 42978, 2771
M 54638, 2955
P 31300, 2771
R 32631, 2765
S 31390, 2843
S 37509, 2824
S 42073, 2904
Sch. 36144, 2562
St. 19374, 2904
V 8974, 2627
V 9653, 2627, 2631
V 9693, 2632
V 11214, 2904
W 30036, 2577
W 30436, 2588
W 30500, 2577, 2588
W 36069, 2685
W 38008, 2588

PATENTS

41507, 2708
80776, 2705, 2709
85329, 2548, 2556, 2721, 2928
86368, 2548, 2556, 2721, 2928
97710, 2709
105347, 2548, 2558, 2639, 2928

112817, 2557, 2558, 2634, 2639, 2640, 2736, 2738
117542, 2712
118052, 2712, 2713
118538, 2542, 2549, 2558, 2929
119636, 2712, 2713
120713, 2549, 2558, 2929
122166, 2712
122272, 2714
123121, 2526, 2559, 2664
123122, 2559
123309, 2829
124408, 2693
127350, 2526
127816, 2713
128119, 2683, 2712
128120, 2682
128956, 2683
129420, 2829
132371, 2701, 2705, 2716
132425, 2690
132605, 2526
134721, 2891
137330, 2520, 2525, 2648, 2680
138783, 2705
139589, 2683, 2710
139669, 2557, 2587, 2641, 2656, 2702, 2928
139738, 2711
139905, 2705
140164, 2682
140263, 2713
140480, 2712
140658, 2713
142832, 2682
142971, 2682
144648, 2682
145106, 2630, 2668, 2669, 2679, 2697, 2698, 2763
150625, 2826
151918, 2630, 2631, 2668, 2679, 2697, 2698, 2763
152111, 2628, 2629, 2630, 2672, 2679, 2686, 2697, 2698, 2745, 2760, 2763
152217, 2843
152432, 2843
152630, 2639
153350, 2560, 2562, 2630, 2663, 2670, 2675, 2686, 2687, 2702, 2721, 2727, 2738, 2754, 2776, 2858, 2930
154657, 2741, 2901
157379, 2745
159524, 2542, 2547, 2561, 2562, 2583, 2630, 2663, 2670, 2675, 2686, 2687, 2702, 2721, 2727, 2738, 2754, 2776, 2826, 2858, 2929
161882, 2526
162239, 2630, 2651, 2696, 2760, 2766, 2860
163103, 2526
163316, 2559, 2591, 2687, 2723, 2929
163668, 2711
166181, 2708
168497, 2713
169364, 2858
169730, 2517
169782, 2688, 2695, 2824, 2828
169930, 2724
170533, 2674
171900, 2730
172931, 2520
172941, 2707
172966, 2709, 2713
172967, 2709
173020, 2713
174001, 2686
174068, 2741
174259, 2709, 2713
174914, 2669, 2715
175379, 2628, 2764, 2796,
175664, 2687, 2695, 2824, 2828
176474, 2706, 2710
177778, 2710
178133, 2698, 2708, 2716
179947, 2648, 2649, 2724
180126, 2706, 2713
180208, 2710
180216, 2706
180666, 2594, 2820, 2930
180667, 2594, 2820, 2930
181784, 2829
182558, 2520, 2525, 2680, 2893
182691, 2517
182773, 2688, 2695, 2824, 2828
184145, 2564, 2670, 2758, 2929
184201, 2564, 2670, 2758, 2842
184229, 2703
185151, 2605, 2613, 2724, 2758, 2763
185240, 2630, 2665, 2666, 2668, 2669, 2700, 2766, 2861
185241, 2630, 2665, 2666, 2668, 2669, 2700, 2766, 2861
185347, 2741
185374, 2750
185808, 2707
185837, 2662, 2663
188542, 2628, 2745, 2796
189703, 2629, 2631, 2672, 2673, 2686, 2697, 2710, 2745, 2760,
189836, 2525, 2620, 2621 2630, 2680, 2681, 2842
189837, 2525, 2620, 2621, 2630, 2680, 2681
191326, 2525, 2667, 2859
193135, 2836, 2837
193210, 2888
193509, 2517
194884, 2734
196324, 2740
196730, 2592, 2930
198008, 2699, 2837
198482, 2543, 2601, 2636, 2721, 2747, 2931
199559, 2699, 2837
200145, 2648
200149, 2648, 2649, 2724
200201, 2651
200334, 2654, 2686, 2739
200916, 2559, 2687, 2723
201233, 2603, 2636, 2698 2931
201705, 2742
201907, 2630, 2703
201910, 2592, 2930
202720, 2630, 2679, 2702, 2766
203178, 2597, 2603, 2635, 2636, 2698, 2771, 2931
203462, 2931
203642, 2543, 2600, 2639
204868, 2866
204883, 2742
204942, 2722
206950, 2597, 2635, 2931
208834, 2730

209268, 2734
209418, 2517
209943, 2690
210502, 2734
210519, 2630, 2651, 2663, 2676, 2686, 2687, 2689, 2721, 2761 2768
210778, 2648, 2649, 2724
211186, 2728
211198, 2703
211199, 2703
211520, 2853, 2885
211573, 2853, 2885
214962, 2711
216070, 2725
216716, 2734
216940, 2734
217554, 2725
219116, 2813
219162, 2620, 2621, 2624
219163, 2620, 2624
219918, 2710
220228, 2629, 2631, 2672, 2673, 2686, 2710, 2745, 2760
220705, 2520
222236, 2526
222450, 2598, 2635, 2663, 2666, 2670, 2676, 2758
222777, 2738
223208, 2521
223793, 2630, 2663, 2676, 2686, 2687, 2689, 2721
224330, 2843
227198, 2822
227238, 2826
227667, 2690
228867, 2630, 2689, 2840
229450, 2811
229536, 2735
229678, 2717
230171, 2517, 2523
231030, 2824
232707, 2517
233589, 2620, 2627
233786, 2595
234028, 2699, 2837
234264, 2734
234580, 2516
235357, 2692
235381, 2312
235752, 2517
236056, 2692
237150, 2678
237151, 2663, 2670, 2869
237210, 2621, 2628, 2841
237599, 2631, 2681
237718, 2520, 2680, 2681, 2821
237765, 2621, 2626
237766, 2621, 2626
238341, 2735
238348, 2664, 2696, 2699, 2736, 2739, 2780, 2783
238361, 2806
239075, 2516
239077, 2736
239697, 2678
239701, 2631, 2681, 2821
240188, 2689, 2823
240751, 2651, 2676, 2747, 2842
241559, 2743
241781, 2806
241898, 2526
241963, 2882
241973, 2718
242289, 2613, 2663, 2670
242467, 2668, 2672, 2694, 2699, 2700, 2766
242612, 2677
242786, 2639, 2676, 2732 2804
243068, 2825, 2826
243225, 2518
243581, 2587, 2641, 2656, 2702
243797, 2518
244602, 2527
244787, 2688
244816, 2522
245168, 2517
245575, 2577
246081, 2765
246242, 2738
246382, 2716
246606, 2724
246651, 2685, 2693
246657, 2685, 2693
246661, 2600,
246967, 2630, 2718
248559, 2651, 2676, 2747, 2842
248946, 2826
248982, 2751, 2753
248984, 2728, 2733
249333, 2522
249535, 2621, 2687
251259, 2716
251351, 2669, 2797
251372, 2703
252661, 2577
252706, 2554, 2567
254069, 2725, 2727, 2728
254083, 2863
254093, 2628
254385, 2665
254709, 2735
254784, 2799
255441, 2588
255692, 2669, 2797
255704, 2581, 2769
255901, 2728
256922, 2561, 2665, 2800
259248, 2654
253879, 2606
260232, 2521
260915, 2801
260984, 2585, 2614
261589, 2522
262092, 2716
263056, 2608, 2683
263106, 2735
263457, 2729
264006, 2725, 2728
265852, 2632, 2633
265911, 2630, 2632, 2633
266384, 2883
266600, 2632, 2633
266781, 2732
267370, 2824
267407, 2682
267487, 2728
267577, 2632, 2633
268489, 2889
268627, 2665, 2800
269193, 2602, 2603, 2821
270314, 2807
270580, 2771
270993, 2956
272121, 2594
272339, 2900
272695, 2855
273029, 2602, 2603, 2821
273101, 2527
273344, 2734
573706, 2581, 2607, 2771
273800, 2508
273979, 2815
274032, 2907
274260, 2573, 2581, 2771
274782, 2729
275049, 2907
275062, 2769
276013, 2693, 2769, 2771
277529, 2883

277605, 2956
279638, 2901
281265, 2956
281304, 2956, 2932
281432, 2956
282263, 2955
283163, 2955

AUSTRIAN

Jan. 1, 1899, 2549
Feb. 4, 1899, 2549
Aug.14, 1909, 2676
Mar.16, 1910, 2607, 2664, 2676
237, 1910, 2595
327, 1911, 2520, 2525, 2633, 2821
403, 1911, 2685, 2693
1642, 1909, 2630, 2823, 2824
1787, 1912, 2587, 2675, 2685, 2686
1793, 1911, 2762
1905, 1909, 2883
2118, 1910, 2684
2376, 1911, 2621, 2628, 2841
2906, 1910, 2811
2907, 1910, 2799
2994, 1911, 2632, 2681, 2696
3034, 1913, 2807
3060, 1909, 2764
4624, 1909, 2685, 2686
4642, 1910, 2689, 2691, 2694, 2695, 2696, 2698, 2699, 2700, 2701, 2702, 2703, 2736, 2825
5012, 1910, 2595
5148, 1910, 2627
5592, 1910, 2664, 2727
5655, 1909, 2762
5896, 1910, 2595
6220, 1910, 2776
8062, 1910, 2602
8165, 1902, 2549, 2883
8334, 1911, 2835
8776, 1910, 2626, 2901
9229, 1911, 2719
9533, 1909, 2630, 2765, 2784
9557, 1903, 2710
9872, 1910, 2631
13838, 1903, 2710
17456, 1902, 2566
21213, 1905, 2901
21614, 2901
25335, 1906, 2713
27060, 1906, 2713
27258, 1910, 2595
31203, 2605
31391, 2561, 2562, 2630, 2663, 2670, 2676, 2686, 2687, 2702, 2721, 2727, 2738, 2754, 2776
32637, 2562, 2664
33508, 1908, 2901
34272, 1908, 2901
34908, 1908, 2672, 2686, 2710, 2761
35015, 2564, 2758
36126, 2592
37138, 2592
41461, 1909, 2567, 2675
41811, 1910, 2901
41831, 1907, 2636, 2864
46036, 2813
42440, 1909, 2559, 2687, 2724
45765, 1909, 2620, 2621, 2624
46991, 1910, 2664, 2676, 2721, 2753
47244, 2640, 2684, 2695, 2696
47889, 2630, 2688, 2690, 2736
47899, 2664, 2696, 2699, 2736, 2739, 2758, 2780, 2783
49177, 2620
50331, 1912, 2595
50656, 1910, 2630, 2666, 2679, 2698, 2761
51094, 1908, 2630, 2663, 2676, 2686, 2687, 2721
52289, 1911, 2595, 2626
53109, 2640, 2684, 2695, 2696
54512, 1912, 2621, 2687
54819, 2620
55443, 1911, 2743
55514, 2782
55527, 2681
55654, 2771
57421, 2620
57984, 2813
60447, 2620
63556, 2835
63966, 2767
64085, 2958
65040, 2771

BELGIAN

113156, 2556, 2721
137577, 2548, 2557, 2558, 2634, 2639, 2640, 2663, 2736, 2738
138462, 2548, 2556, 2558, 2634, 2663, 2736, 2738
171743, 2520, 2525, 2680, 2893
177234, 2723
177235, 2723
177236, 2723
181194, 2766
182050, 2766
182216, 2564, 2758
183877, 2593
184896, 2707
185701, 2517
187308, 2567, 2675
188838, 2518
190920, 2708
191531, 2706
194836, 2705
194975, 2735
195098, 2891
195837, 2525, 2859, 2667
195839, 2593, 2697, 2822
195840, 2745, 2796
198836, 2859
198984, 2620, 2621, 2624
198985, 2620, 2621, 2624
199492, 2592, 2600
200494, 2708
200926, 2742
201017, 2766
205575, 2742
209561, 2885
214671, 2681
216668, 2765, 2784
216918, 2725
217837, 2620, 2621, 2624
218192, 2875
219502, 2526
219909, 2526
220225, 2825
222106, 2630, 2666, 2679,

2698, 2762
223996, 2640, 2684, 2695, 2696
224950, 2578
226582, 2595
227385, 2595
229046, 2620
229396, 2806, 2883
229995, 2602, 2621, 2626
231853, 2621, 2687
232475, 2520, 2525, 2821
232699, 2685, 2693
233786, 2621, 2628, 2841
233792, 2620
234433, 2620, 2627
239564, 2565, 2621, 2625, 2640, 2641, 2658
241116, 2719, 2762
241250, 2607, 2629, 2664, 2676
241251, 2629, 2630, 2666, 2668, 2669, 2671, 2679, 2689, 2695, 2696, 2697, 2702, 2728, 2732, 2737, 2766
241252, 2630, 2695, 2697, 2701, 2732, 2753
241975, 2762, 2902
242325, 2903
243162, 2903
244470, 2605
244950, 2901
245532, 2825
46250, 2607, 2664, 2676
246251, 2607, 2664, 267J,
246562, 2842
248907, 2565, 2901
250816, 2740
251010, 2595
251011, 2596
252594, 2679, 2767
252882, 2596
253353, 2581
253945, 2654
254591, 2505
259019, 2771
259277, 2746
261288, 2903
261693, 2903

CANADIAN

62042, 2858
62188, 2558, 2663, 2736, 2738
63101, 2557, 2634, 2639, 2640, 2736, 2738
90848, 2567
103036, 2705
103045, 2567, 2675
107996, 2888
129265, 2664, 2696, 2699, 2736, 2739, 2780, 2783
129983, 2668, 2669, 2701, 2736
132232, 2739
133197, 2620
134164, 2621, 2687
136538, 2630, 2639, 2718
139046, 2606
143330, 2522
147424, 2740
147578, 2679, 2767
147579, 2679, 2767
155724, 2768

DANISH

2558, 2557, 2634, 2639, 2640, 2736, 2738
2636, 2558, 2663, 2736, 2738

HUNGARIAN

APPLICATIONS

2966, 2762
E 1568, 2595
G 3096, 2762
G 3210, 2762
G 3306, 2620, 2627, 2762
K 3937, 2762
K 5168, 2769
M 3691, 2630, 2666, 2679, 2698, 2762
M 3798, 2762
N 952, 2620, 2621, 2624
O 674, 2587, 2675, 2685, 2686
R 2398, 2630, 2762, 2765, 2784
S 6073, 2762
W 2976, 2719
W 3204, 2719, 2762

PATENTS

Nov. 8, 1898, 2549, 2558, 2663, 2736, 2738
Aug. 31, 1898, 2549, 2558, 2663, 2736, 2738
3096, 2621, 2687
35866, 2567, 2675

ITALIAN

Apr. 17, 1905, 2593
vol. 215, 1905, 2567, 2675
28964, 2504
31391, 2858
47889, 2664
62042, 2560, 2562, 2630, 2663, 2670, 2676, 2686, 2687, 2702, 2721, 2727, 2738, 2754, 2776
101262, 2520, 2680, 2682, 2821
103978, 2620, 2621
120751, 2565

LUXEMBOURG

3302, 2549, 2558, 2663, 2736, 2738
3361, 2549, 2558, 2663, 2736, 2738
7610, 2558, 2663, 2736, 2738

NORWEGIAN

7610, 2558, 2663, 2736, 2738
16873, 2742

PORTUGUESE

2899, 2558, 2663, 2736, 2738
2930, 2557, 2634, 2639, 2640, 2736, 2738
7102, 2630, 2765, 2784
8348, 2607

RUSSIAN

3264, 2557, 2634, 2639, 2640, 2736, 2738

3378, 2558, 2663, 2736, 2738
7848, 1903, 2682
8855, 1904, 2683
8893, 1904, 2682
11492, 2564, 2670, 2758

SWEDISH

10976, 2762
20249, 2564, 2670, 2758
33546, 2588

SWISS

43330, 2762
46329, 2883
48975, 2825
51644, 2640, 2684, 2695, 2696
51839, 2630, 2666, 2679, 2698, 2762
51910, 2640, 2684, 2695, 2696
51952, 2901
52115, 2664, 2696, 2699, 2736, 2739, 2780, 2783
52273, 2595
52437, 2630, 2664, 2688, 2690, 2736, 2758
52438, 2664, 2676, 2721, 2753
52903, 2901
53777, 2621, 2631, 2687
53888, 2595
54497, 2602, 2621, 2626
55942, 2762
55752, 2743
57952, 2595
61929, 2691, 2881
61930, 2958
62720, 2522
63584, 2768
63585, 2689, 2768, 2901
63586, 2583
65057, 2901
67113, 2957
67258, 2956

INDEX OF NAMES

Compiled by

DEAN S. WORDEN

Aboulene, J., *see* J. Senderens.
Ach, L., and C. Boehringer & Soehne, 2711.
Acker, C., 2723.
Actiengesellschaft, *see* Aktiengesellschaft.
Adams and McKay, 2814.
Aktiengesellschaft fur Anilin Fabrikation, *see* also Berlin Aniline Co.
Aktiengesellschaft fur Anilin Fabrikation, 2527, 2577, 2601, 2625, 2636, 2652, 2654, 2658, 2706, 2720, 2721, 2746, 2811, 2835, 2836, 2884, 2901, 2931, 2955.
Alby Carbidfabr. Aktiebolag, 2742.
Althausse, 2928.
Althausse, M., 2526, 2559.
American Cellone Co., 2789.
Andes, L., 2725.
Anthony, F., 2866.
Anthony, R., 2866.
Arbezcarme, L., 2710.
Armstrong, *see* Fisher.
Armstrong, E., *see* Fischer.
Armstrong, 2589.
Askenasy, P., R. Leiser and N. Gruenstein, 2521.
Askenasy, P., and M. Mugdan, 2725, 2740.
Askenasy, P., and C. Vogelsohn, 2725.
Assadas, S., 2711.
Auerbach, F., and W. Pluddemann, 2906.
Aufrecht, A., *see* H. Grossmann.
Aylesworth, J., 2711, 2747, 2880.
Bachrach, D., 2688.
Bacigalupi, A., 2899.
Badische Anilin & Soda Fabrik, 2518, 2563, 2596, 2691, 2706, 2710, 2713, 2716, 2797, 2904, 2929.
Baechlin, P., 2677.
Baker, H., *see* E. Haworth.
Balland et Cie, 2863.
Balser, W., 2810.
Balston and Briggs, 2721
Bamberger, E., 2528.
Barbier, H., *see* A. Lumiere.
Barboni, E., 2758.
Bardy, 2907.
Bardy, C., 2536.
Barrier, E., 2757.
Barthelemy, H., 2924.
Bary, P., 2747.
Baskerville, C., and H. Riederer, 2722.
Basler, J., & Co., 2707.
Battegay, M., *see* J. Heilman.
Battegay, 2788.
Baumann, 2655.
Baumstark, 2589.
Bayer, F., & Co., *see* A. Eichengruen.
Bayer & Co., *see* Farbenfabriken vorm. E. Bayer & Co.
Beadle, *see* Cross.
Beatty, W., 2679, 2767, 2904, 2909.
Bebie, *see* G. Lunge.
Beck, W., 2921.
Becker, J., 2674.
Becker, T., *see* A. Eichengruen.
Becker, T., 2727.
Bedford, C., and J. and J. Kirk, 2903.
Bedford, J., *see* Bedford, C.
Behal, A., 2707.
Behrend, L., 2694, 2766.
Behrens, A., 2521.
Behrens, J., 2520, 2907.
Belnisch, H., 2901.
v. Belotini, G., 2522.
Beltzer, F., 2774, 2817, 2818, 2831.
Beltzer, J., 2539.
Bemberg, J. P., Aktiengesellschaft, 2634.
Benjamin, G., 2670.
Benesch, E., *see* R. Kremann.
Benrath, P., E. Damm and O. Stephani, 2825.
Berger, E., 2703.
Berl, E., 2504, 2654, 2748.
Berl, E., and W. Smith, 2548, 2623, 2648, 2649, 2650.
Berlin Aniline Co., *see* also Aktien Gesellschaft f. Anilin Fabrikation.
Bernard, R., 2540, 2817.
Berthelot, A., 2735, 2738.
Berthelot and Jungfleisch, 2728, 2739.
Bertram, 2931.
Betteridge, F., *see* Frankenburg, Ltd.
Bevan, E., *see* C. Cross.
Bigot, A., 2736.
Biron, 2757.
Blanksma, J., 2539.
Blavinhac, A., 2747.
Bloch, *see* Persoz.
Blumer, E., 2525, 2648.
Blumer, L., 2525.
Bock, J., 2903.

Bodart, A., 2616.
Boehringer & Soehne, *see* L. Ach.
Boehringer & Soehne, 2711.
Boesch, 2928.
Boesch, B., 2562.
Boeseken, J., 2729.
Boessneck, P., 2521.
Bolis, R., 2724.
Bonhoeffer, O., H. Guntrum and Farb., F. Bayer & Co., 2621.
Bonwitt, C., 2869.
Bonwitt, G , 2628, 2871.
Borinski, *see* Prandtl.
Boroid, Ltd., 2789.
Borzykowski, B., 2842, 2859, 2815.
du Bosc, *see* also Dubosc.
du Bosc, A., 2760.
Bosnische Elektrizitaets-Akt, 2955.
Bouchardat, G., 2615.
Bouchard-Praceiq, E., 2846.
Boucheron, V., 2724.
Bouffort, M., 2724, 2956.
Bourgoin, E., 2735.
Bousfield, R., and T. Lowry, 2523.
Bousfield, W., and T. Lowry, 2522.
Bowman, F., 2540.
Brand, K., 2600.
British Thomson-Houston Co., 2847.
Brandenburg, H., 2742.
Breteau, P., and H. Leroux, 2716.
Briggs, 2655.
Briggs, *see* Balston.
Briggs, J., *see* C. Cross.
British Xylonite Co., *see* J. Goldsmith.
Bronnert, E., *see* Internationale Celluloseester Ges.
Bruce, John W., 2961.
Brueckner, W., 2806.
Bruehl, 2544.
Bruehl, E., *see* A. Henning.
Bruening, *see* Meister.
Buchemin, R., *see* L. Pages.
Bucher, J., 2519.
Buchk, 2535.
Buettner and Neumann, 2541, 2542.
Bume, F., 2721, 2761.
Byasson, H., 2729.
Byk, H., *see* Chemische Werke.
Cain, J., 2711.
Caines, C., *see* P. Squire.
Callan, J., *see* E. Thomson.
Callenberg, E., 2707.
Calvert, G., 2521, 2907, 2955.
Cameron, F., 2524.
Campbell, A., 2854.
Camphre, *see* Le Camphre.
Camus, E., *see* L. Pages.
Capp, F., 2880.
Carius, 2589.
Carius, L., 2735.
Cathelineau and Fleury, 2700, 2861.
Celluloid Co., *see* W. Lindsay.
Celluloid Co., 2692.
Chalmers, H., 2901.
v. Charante, J., 2616.
Charuel, Y., 2770.
Chattaway, F., 2905.
Chaubet, J., 2712, 2866.
Chauvet, H., 2817.
Chemical Society Industrie Basle, 2516.
Chem. Fab. auf Actien, 2579, 2580, 2582, 2595, 2733.
Chemische Fabrik Buckau, 2729.
Chemische Fabrik Griesheim Elektron, 2517, 2521, 2710, 2725, 2727, 2729, 2731, 2735, 2740, 2742, 2796.
Chemische Fabrik, Grunau, Landshoff and Meyer Akt. Ges., 2517.
Chemische Fabrik, Grunau, Landshoff, Meyer, E. Franke and W. Kirchner, 2518.
Chemische Fabrik von Heyden Aktiengesellschaft, 2577, 2602, 2633, 2686, 2693, 2735, 2821, 2885.
Chemische Fabrik Weiler-ter-Meer, 2705, 2709, 2715.
Chemische Werke vorm. H. Byk, 2800, 2903.
Chevalier, C., and A. Lejeune, 2502.
Churrel, 2882.
Cie Urbaine d'Eclairage par le Gaz Acetylene, 2522.
Claessen, C., 2598, 2635, 2666, 2670, 2698, 2703, 2707, 2708, 2709, 2711, 2713, 2716.
Claus, A., and Nahmacher, 2738.
Clausnitzer, 2589.
Clayton Aniline Co., *see* H. Tompkins, 2729.
Clement, L., and C. Riviere, 2540, 2689, 2748, 2774, 2793, 2797, 2818, 2904.
Cochius, 2918.
Cohoe, W., 2903.
Colin, A., 2817.
Collardon, L., 2672, 2731, 2772.
Colles, 2525.
Collischon, P., F. Ruppert and Verein. f. Chem. Ind., 2903.
Colson, A., and H. Gautier, 2740.
Combes, A., 2735.
Combes, A. and P., 2722.
Combes, C., 2723.
Combes, P., *see* A.
Committee of Economic Arts of France, 2536.
Compagnie Francaise des Applications de la Cellulose, 2834.
Compagnie Francaise du Celluloid, 2690, 2700.
Compagnie Generale d'Electricite, 2855.
Compagnie Generale des Etablissment Pathe Freres, 2956.
Compagnie Generale de Phonographe, Cinematographie et Ap-

Compagnie Generale de Phonographe, Cinematographie et Appareils de Precision, 2691, 2881.
Comp. Gen. des Etabl. Pathe Freres, 2956.
Compagnie Industrielle des Alcools de l'Ardeche, 2521.
de Conick, *see* Oechsner de Conick.
Connor, C., and J. Stubbs, 2724.
Consortium *see* Konsortium.
Convert, G., 2749.
Corti, A., and Fabrique de Produits, Chimiques Flora Societe Anonyme, 2593.
Cossitt, F., 2866.
Costley-White, K., *see* J. Lyndall.
Cote, E., 2721, 2723.
Cote, E., and P. Pierron, 2723.
Crefelder Seifenfabrik Stockhausen and Traiser, 2750.
Crocker, J., 2721.
Crockett, C., 2717.
Cross, C., *see* C. Weber.
Cross, C., 2721.
Cross, C., and E. Bevan, 2533, 2534, 2536, 2547, 2548, 2549, 2556, 2567, 2622, 2644, 2655, 2843, 2888, 2923, 2928, 2931, 2945, 2947.
Cross, Bevan and Beadle, 2655.
Cross, Bevan and Briggs, 2644, 2653, 2654.
Cross, Bevan and Jenks, 2655, 2944.
Cross, Bevan and Traquair, 2646, 2893.
Cross, C., and J. Briggs, 2843.
Cross, C., and J. Traquair, 2525, 2893.
Cullum, H., *see* H. Peters.
Daly, J., 2803, 2804.
Damm, E., *see* P. Benrath.
Dammann, E., 2904.
Daniels, W., 2871.
Danzer, H., 2576, 2666, 2689, 2863, 2867, 2870, 2875.
Danziger, J., 2723.
Davidson, E., 2724.
Davis, J., *see* W. Dreaper.
Davoine, H., 2957.
Debauge et Cie, 2613.
Deglatign, L., and M. Jonas, M. Desmonts and L. Dubosc, 2522.
Deiss, A., and C. Fournier, 2909.
Delahaye, H., 2909.
Deligeon, E., *see* C. de la Gabiniere.
Deming, H., 2625.
Denayrouze, L., 2891.
Denham, W., and H. Woodhouse, 2508, 2897.
Denis, H., *see* O. Dubosc.
Descude, 2931.
Desmonts, M., *see* L. Delatign.
Desvaux, *see* Societe Neumann.
Desvaux, L., 2748.
Deutsche Gasgluelicht Akt. Ges., 2903.
Deutsche Sprengstoffe Actiengesellschaft, 2735.
Deutsche Zelluloid Fabrik, *see* R. Muller.
Deutsche Zelluloid Fabrik, 2701, 2705, 2716.
Dieterich, H., *see* E. Knoevenagel.
Dittmar, H., 2883.
Dixon, W., 2897.
Dobereiner, 2589.
Doerfiinger, W., 2717, 2718, 2722, 2801.
Doht, W., 2817, 2854.
Dolter, *see* Societe, D'Exploitation des Brevets Dolter.
Donard, E., and H. Labbe, 2716.
Douque, A., 2806.
Dreaper, W., 2817.
Dreaper, W., and J. Davis, 2817.
Dreyfus, C., 2594, 2595, 2626, 2723.
Dreyfus, H., 2507, 2526, 2583, 2586, 2607, 2613, 2671, 2691, 2701, 2728, 2753, 2768, 2821, 2899, 2901, 2903, 2956, 2957.
Dreyfus & Co., 2789.
Drucker, K., and R. Kassel, 2523.
Dubosc, *see* also, du Bosc.
Dubosc, A., 2519, 2623, 2638.
Dubosc, L., *see* L. Deglatign.
Dubosc, O., A. Luttringer and H. Denis, 2516, 2519.
Duchaux, J., 2825.
Dunstan and Thole 2525.

Eastlake, W., 2909.
Eastman Kodak Co., 2754, 2860.
Eastman Kodak Co., *see* also D. Reid.
Eberstadt, 2950.
Eberstadt, O., 2925.
Eder, 2544.
Edwards, B., 2866.
Edwards, M., *see* K. Orton.
Edwards, M., and K. Orton, 2909.
Egger, F., *see* H. Franzen.
Eichengruen, A., 2536, 2539, 2543, 2547, 2554, 2660, 2665, 2673, 2690, 2701, 2746, 2768, 2774, 2776, 2780, 2781, 2782, 2783, 2784, 2799, 2811, 2813, 2817, 2818, 2886, 2889, 2901, 2902. 2958.
Eichengruen, A., and F. Bayer & Co., 2595.

Eichengruen, A., and T. Becker, 2560, 2774, 2775, 2777, 2958.
Eichler, T., *see* O. Schmidt.
Escales, 2945.
Eisenlohr, F., 2523, 2675, 2677.
Eisenmann, *see* Zuehl.
Ekeley, J., and C. Slater, 2909.
Ekstroem, P., 2588.
Elektrochemische Werke, 2518.
Elektrochemische, etc., *see* Konsortium.
Ellis, C., 2725, 2633, 2673, 2766.
Engelskirchen, P., 2588.
Erdmann, 2589.
Erwig, E., and W. Koenigs, 2533, 2616.

Faber and Tollens, 2567.
Farb. F. Bayer & Co., *see* O. Bonhoeffer.
Farbenfabriken vormals F. Bayer & Co., 2516, 2520, 2526, 2541, 2542, 2554, 2560, 2567, 2572, 2576, 2577, 2595, 2648, 2665, 2667, 2685, 2691, 2702, 2703, 2721, 2727, 2762, 2765, 2774, 2787, 2800, 2812, 2820, 2823, 2825, 2826, 2829, 2858, 2891, 2892, 2896, 2901, 2929, 2930, 2931.
Fabriek van Chemischen Produkten, 1957.
Fabrik Chemische Praeperata von Dr. R. Sthamer, 2559.
Farb. v. Meister Lucius, and Bruening, 2907, 2955.
Fabrique de Produits Chimiques Flora Societe Anonyme, 2593.
Faraday, 2734, 2764.
Farbwerke vorm. Meister Lucius & Bruening, 2517, 2907.
Farrell, J., 2895.
Fauconnier, A., and J. Sanson, 2736.
Faust, 2528.
Faust, C., 2524, 2726.
Febvre, J., 2723.
Feitler, S., 2825.
Fernbach, A., and E. Strange, 2674.
Feval, L., 2814.
Fichtmueller, J., 2802.
Field, W., 2814.
Fils Pinay, *see* Les Fils Pinay.
Firma L'Emaillite, 2885.
Fischer, E., 2539, 2616, 2703, 2728, 2748, 2817.
Fischer and E. Armstrong, 2615.
Fisher, L., *see* A. Huck.
Flemming, 2727, 2737.
Flemming, R., 2849.
Fleury, A., *see* H. Cathelineau.
Flooh, A., *see* R. Kremann.
Florentin, D., 2652.
Foerg, R., 2615.
de Forcrand, R., 2525.
Forrest, C., *see* C. Richardson.
Forster, A., 2826.
le Fortier, G., 2891.
Fournier, C., *see* A. Deiss.
France, J., 2554, 2568.
Franchimont, 2509, 2532, 2533, 2534, 2598, 2928, 2929, 2943.
Franke, E., *see* Chem. Fab. Grunau.
Frankenburg, R., *see* Frankenburg, Ltd.
Frankenburg, Ltd., R. Frankenburg and F. Betteridge, 2750.
Frankfort, F., 2739.
Frankhausen, I., 2648.
Franquet, E., 2705.
Franzen, H. and F. Egger, 2906.
Franzen, H. and G. Greve, 2906.
Fraps, G., 2719.
Frederking, H., 2816.
Freiss, 2931.
French, E., 2522.
French, E. and J. Withrow, 2907.
de la Fresnaye, P. and E. Cadoret de la Gabiniere, 2674.
Friedmann, E., 2841.
Furst Guido Donnersmarck'sche, Kunstseiden u. Acetatwerke, 2631, 2634, 2653, 2680, 2821, 2829, 2840, 2843, 2883.

de la Gabiniere, E., *see* P. de la Fresnaye.
de la Gabiniere, C. and E. Deligeon, 2674.
Garner, J., B. Saxton and H. Parker, 2519.
Gautier, *see* Colson.
Gautier, A., 2615.
Gawlich, G., 2813.
Geinsperger, E., *see* Skraup.
Genequand, P., *see* A. Pictet.
Genequand, P., 2649.
General Chemical Co., 2955.
General Electric Company, 2849, 2851.
Gerin, F., *see* Guerin, F.
Geuther, 2589.
Geuther, A., 2735.
Geutner, 2931.
Gillet, C., 2710.
Gilliard, P., Monnet et Cartier, *see* Societe Chimique des Usines.
Girard, 2541, 2542, 2558, 2615.
Girard, A., 2531.
Girard, P., 2504.
Girzik, 2932.
Girzik, E., 2807.
Glaser, C., 2757.
Glock, G., 2523.
Gmelin, 2589.
Goldberg, E., 2733.
Goldman, 2782.
Goldschmidt, T., 2526.
Goldsmith, B., 2814.
Goldsmith, G., 2714.
Goldsmith, J., and British Xylonite Co., 2711.
Goldstein, K., 2813.

Gonon, C., *see* Societe Generale des Films.
Goodwin, H., 2865.
Goodwin, W., *see* L. Macquenne.
Gowing-Scopes, L., 2720, 2733.
Graefe, E., 2721.
Green, 2548, 2931, 2932.
Green, A., 2539.
Green, A. and A. Perkin, 2539, 2548, 2649, 2921.
Gregory, H., 2802.
Greve, H., *see* H. Franzen.
Groschuff, E., 2757, 2758.
Groshuff, *see* Groschuff.
Grossmann, H., and A. Aufrecht, 2905.
Grote, L., 2566, 2770.
Gruenstein, *see* P. Askenasy.
Guerin, *see* L. Vignon.
Guido Henckel Donnersmarck, *see* Furst Guido, etc.
Guignard, G., 2909.
Guignard. G., *see* G. Periere.
Guignet, C., 2532.
Gulberg and Waage, 2551.
Guntrum, *see* O. Bonhoeffer.
Gutmann, 2945.
Gutsch, Jesse, 2927.

de Haas, T., 2567.
de Haas, T. and Tollens, 2567.
Haberland, H. and W. Schaefer, 2751.
Haeussermann, 2930.
Haeussermann, C., 2537, 2648.
Hagemann, E., 2729.
Hake and Lewis, 2654.
Hamburger, H., *see* Z. Skraup.
Hamel, M., 2516.
Hardcastle, J. and A. Taylor, 2956.
Hardt - Stremayr, E., 2510, 2537.
Harris, J., 2887.
Hartwig, K., 2519.
Hassack, 2831.
Hassack, A., 2818.
Hassack, C., 2830.
Hauser, O., and H. Muschner, 2655, 2657.
Haworth, E., and H. Baker, 2723.
Heilman, J., & Co., H. Wagner and M. Battegay, 2787, 2788.
Heine & Co., 2690.
Heintz, W., 2717.
Heitz, see Societe Leduc,
Heller, G., 2693.
Hempel, A., 2517, 2519.
Henckel - Donnersmarck, *see* also Fuerst Guido Henckel-Donnesmarck.
Henckel - Donnersmarck, 2549, 2558, 2928.
Henderson, *see* Scott.
Hennings, C., 2775.
Henning, A. and E. Bruehl, 2722.
Henri, V., 2863.
Henry, V., 2918.
Heraud, R., *see* L. Nottelle.
Herz, W., 2757.
Herz, W. and W. Rathmann, 2719, 2722, 2730, 2739, 2743, 2752.
Herzfeld, 2616.
Herzog, A., 2817, 2818, 2827, 2830, 2831, 2832.
Heumann and Kochlin, 2589.
Hewitt, P., 2863.
v. Heyden, *see* Chem. Fabr. v. Heyden.
Hill, T., 2722.
Hinsberg, 2535.
Hirsch, J., 2761, 2856.
Hirzel, H., 2757.
von Hochstetter, H., 2521.
Hoefer, F., and M. Mugdan, 2743.
v. Hoehnel, 2831.
Hoemberg, R., 2576.
Hoenes, H., 2882.
Hoermann, O., *see* C. Liebermann.
Hoesch & Co., 2909.
Hofmann, K., 2822.
Hofmann, K., and E. Seiler, 2754.
Hoffmann, A., 2717.
Hoffsummer, I., 2858.
Hoitsema, 2945.
Hontsch & Co., 2678.
Hottenroth, V., 2922.
Howard, H., 2516, 2518.
Hubbard, J., 2523, 2675.
Hue, G., 2866.
Hubener, G., 2882.
Hubner, 2931.
Hubner and Muller, 2736, 2754.
Huck, A., and L. Fisher, 2802.
Huneke Maschinenbau, *see* Martini.

Ichenhauser, E., 2769.
Imbert, G., 2728.
Imbert and Konsortium fuer Elektrochemische Industrie, 2734.
Internationale Celluloseester Gesellschaft, 2585, 2613, 2626, 2630, 2663, 2882.
Internationale Celluloseester Ges., and E. Bronnert, 2663.

Jacquet, 2576.
de Jahn, F., 2909.
Jenks, *see* Cross.
Johnson, E., 2757.
Jones, 2905.
Jones, M., *see* K. Orton.
Joseph, A., 2905.
Jouas, M., *see* L. Deglatign.
Jungfleisch, *see* Berthelot.

Kahlbaum, C., 2528.
Kalle & Co., 2708.
Kassel, R., *see* K. Drucker.

Katayama, T., *see* H. Ost.
Kennedy, A., 2814.
Ker, W., 2802.
Kerschbaum, F., *see* R. Kremann.
Kessler, H.. 2526.
Kilmer, F., 2504.
King, H., *see* M. Edwards.
King, H., *see* K. Orton.
Kingzett, C., 2522.
Kingzett, C., and R. Woodcock, 2518.
Kirchhoff, G., *see* W. Steinkopf.
Kirchner, W., *see* Chem. Fabr. Grunau.
Kirk, J., *see* Bedford, C.
Klatte, F., 2685.
Kldiaschwili, 2546.
Klein, 2513, 2542, 2543.
Klein, F., *see* H. Ost.
Klein, F., 2510, 2905, 2909.
Knaster, M., 2814.
Knoevenagel, 2931, 2955.
Knoevenagel and Dieterich, 2955.
Knoevenagel, E., 2538, 2546, 2594, 2837, 2903, 2957, 2958.
Knoevenagel, E., and v. Martins, 2955.
Knoevenagel, K., 2513, 2598.
Knoll & Co., 2541, 2573, 2577, 2578, 2581, 2590, 2594, 2595, 2597, 2600, 2603, 2607, 2635, 2639, 2693, 2769, 2771, 2820, 2837, 2864, 2900, 2930, 2957, 2958.
Knorr, *see* Koenigs.
Kochlin, *see* Heumann.
Koenig, J., *see* Z. Skraup.
Koenigs, W., *see* E. Erwigs.
Koenigs and Knorr, 2616.
Kgl. Materialpruefungsamt, 2957.
Koepp R. & Co., 2516.
Koerner, 2541, 2542.
Koller, 2667.
Koller, G., 2732, 2743, 2750, 2902.
Koller, H., 2732.
Konchine, *see* Societe des Manufactures.
Konowalow, 2589.
Konsortium, *see* also Consortium.
Konsortium fur Elektrochemische Industrie, *see* Imbert.
Konsortium f. Elektrochemische Industrie. 2522, 2725, 2730, 2733, 2740, 2741, 2742, 2743, 2749, 2907, 2909.
v. Kraffl - Lenz, *see* Skraup.
v. Kraffl-Lenz, E., 2616.
Krafft, F. and V. Merz, 2755.
Krauschwitzer, Thonwaarenfabrik fur Chem. Ind., 2523.
Kremann, R., *see* Z. Skraup.
Kremann, R., 2616.
Kremann, R., Benesch, Flooh and Kerschbaum, 2525.
Kruemmling, M., 2805.
Kruger, G., 2724.
Kuertz, 2802.

Laarmann, F. 2886.
Labbe, H., *see* E. Donard.
Lagrange, P., 2762, 2855.
Lance, R., *see* C. Schrager.
Landolt, 2914.
Landrum, R., 2523.
Landsberg, L., 2566.
Landshoff, *see* Chem. Fabr. Grunau.
Lasche, A., *see* C. Schroeder.
"La Solvea," *see* Societe Anonyme par Acatiens.
Lassieur, A., 2677.
Laudien, E., *see* C. Schraube.
Laurent, A., 2754.
Law, D., 2548, 2644.
Lebach, H., 2817.
Le Camphre, *see* also Societe Anonyme Le Camphre.
Lederer, L., 2525, 2541, 2542, 2555, 2558, 2559, 2578, 2593, 2605, 2610, 2613, 2636, 2640, 2648, 2649, 2651, 2667, 2668, 2672, 2692, 2693, 2697, 2723, 2724, 2745, 2747, 2760, 2762, 2763, 2764, 2775, 2796, 2820, 2822, 2842, 2859, 2860, 2929, 2958.
Leduc, Heitz & Co., 2806.
de Leeuw, 2757.
Lefferts, M., *see* J. Stevens.
Lehmann, F., 2903, 2956.
Leiser, R., *see* P. Askenasy.
Lejeune, A., *see* Chevalier, C.
Lemaire, E., 2900.
Leman, P., 2766.
Lender, R., 2956.
Leroux, H., *see* P. Breteau.
Les Fils Pinay jeune, *see* P. Prost.
Leuchter, 2782.
Levi, L., *see* C. Schroeder.
Lewis, *see* Ramsey.
Leys, 2906.
Lidholm, J., 2742.
Lieben, 2906.
Liebermann, C., 2532.
Liebermann, C. and O. Hoermann, 2531.
Lilienfeld, L., 2505, 2508, 2593, 2695, 2809, 2824, 2828, 2900, 2901.
Lindet, M., 2531.
Lindsay, W., 2683, 2684, 2691, 2697, 2701, 2703, 2737, 2739, 2753, 2761, 2767, 2770, 2932.
Lindsay, W. and Celluloid Co., 2708.
L'Industrie Chim. Bale, *see* Societe pour L'Industrie Chim. Bale.

Little, A., *see* H. Mork.
Little, A., 2525, 2845.
Loewonthal, R., 2817.
Longmate, W., 2900.
Loose, A., *see* Chem. Fab. auf Aktien.
Loose, A., 2595.
Lourenco, A., 2738.
Lowry, T., *see* Bousfield.
Lucius, *see* Meister.
Luck, A., 2658, 2846.
Lumiere, A., 2863.
Lumiere, A. and L., 2880, 2881.
Lumiere, A. and L., and H. Barbier, 2527, 2528.
Lumiere, L., *see* A. Lumiere.
Lumiere, A. et ses Fils. same as Lumiere & Sons.
Lumiere, A. & Sons, 2764, 2867.
Lunge, 2544, 2550.
Lunge, G. and Bebie, 2544.
Lunge and Weintraub, 2544, 2945.
Luttringer, A., *see* O. Dubosc.
Lutz, G., *see* O. Schmidt.
Lyndall J. and K., Costley-White, 2757.

McClellan, J., 2710.
McKay, *see* Adams.
MacKaye, J., 2722, 2723.
McTavish, Ramsey & Co., 2855.
Maas & Waldstein Co., 2739.
Machalske, F., 2723.
Macquenne, L. and W. Goodwin, 2509.
Maeder, H., 2906.
Mailhe, A., *see* P. Sabatier.
Main, W., 2539, 2748, 2817.
Malosse, H., 2523, 2722.
Manissadjian, H., *see* W. Merckens.
Manissadjian, H., 2689, 2672.
Marckwald, L., 2520.
Marsden, 2539, 2845.
Marsden, F., 2537, 2817, 2818.
Martens, A., 2816.
Martini and Huneke Maschinenbau, 2757.
v. Martius, *see* E. Knoevenagel.
Marx, *see* Societe Neumann.
Maschke, A., 2682.
Masland, W., *see* F. Sparre.
Masson, O., 2504.
Massot, W., 2817, 2818, 2830, 2832.
Matthews, J., 2723.
Matthews, M., 2539.
Mayser's Hutfabrik, 2815.
Maywald, F., 2723.
Meister, Lucius & Bruening, 2714.
Mendeleeff, 2544.
Menter, F., *see* Skraup.
Mentschutkin, 2618.
Mentschutkin and Wasiljeff, 2917.
Merckens, W., *see* J. Smith.
Merckens, W. and H Manissadjian, 2684.
Merz, V., *see* F. Krafft.
Meunier, G., 2909.
Meyer, *see* Chem. Fabr. Grunau.
Meyer, F., 2651, 2888.
Meyer, G., 2762, 2771.
Meyer, J., 2525.
Michael, A., 2643.
Michaelis, 2589.
Michel, 2741.
Michel, F., 2754.
Mijnessen, C., 2761, 2762.
Miles, G., 2539, 2553, 2554, 2567, 2569, 2634, 2929.
Militz, A., 2896.
Minck, P., 2502.
Minuto, J., *see* D. Young
Mitteilungen d. Techn. Gewerbemuseum Wien, 2585.
Molinari, U., 2906.
Moncany, G., 2899.
Morane, L., *see* J. Schmerber.
Moreul, T., 2503.
Morford, J., *see* Viscose Development Co.
Mohr, O., 2866.
Mork, H., 2540, 2541, 2584, 2605, 2612, 2693, 2822, 2840, 2861, 2862, 2923.
Mork, H., A. Little and W. Walker, 2590, 2819.
de Mosenthal, 2547.
Mouneyrat, A., 2740.
Moureau, 2589.
Mugdan, M., 2521.
Mugdan, M., *see* P. Askenasy.
Mugdan, M., *see* E. Hoefer.
Mueller, A., *see* J. Mueller.
Mueller, E., 2737.
Mueller, J and A., 2521.
Muller, *see* Hubner.
Muller, R. and Deutsche Celluloid Fabrik, 2908, 2955.
Muntz, W., 2900.
Muschner, H., *see* O. Hauser.
Muschner, H., 2543.

Naamlooze Vennootschap Fabrik van Chem. Produkten, 2527, 2907, 2912, 2955.
Nagel, O., 2707.
Nahmacher, *see* A. Claus.
Nastjukoff, A., 2657.
Nastukoff, 2567.
Naudin, L., 2530.
Netz, C. & Co., 2728.
Neumann, *see* Buettner.
Neumann, *see* Societe Neumann.
Neumann, M., 2518.
Nishida, H., 2652.
Nitritfabrik Akt., 2624 2762.
Nitrit Fabr. Bemberg, 2680, 2681.

Nitritfabrik Copenick, 2517.
Nitzelnadel, K., 2504.
Niviere, J., 2736, 2738.
Norris, W., 2906.
Nottelle, L. and R. Heraud, 2882, 2885.
Nowalk, C., 2724.
Noyer, G., 2540, 2689, 2690, 2918.

Obermuller, 2590.
Oechsner de Conick, W. and A. Raynaud, 2648.
Oeser, E., 2803.
Ogier, 2589.
Oglialoro, *see* Paterno.
Olsen, K., 2802.
Ornstein, G., 2527, 2742, 2743.
Orton. K., *see* M. Edwards.
Orton, K., *see* A. Smith.
Orton, K., M. Edwards and H. King, 2522, 2525.
Orton, K. and M. Jones, 2528.
Ost, 2541, 2542, 2543, 2545, 2649, 2932.
Ost, H., 2502, 2513, 2536, 2547, 2922.
Ost, H. and T. Katayama, 2511, 2543.
Ost, H. and F. Klein, 2521, 2656.
Ottorepetz, O., 2834.

Pages Camus et Cie, *see* also Societe Pages Camus et Cie.
Pages Camus et Cie, 2677.
Pages, L., E. Camus, R. Buchemin and Soc. Pages Camus et Cie, 2674.
Pantjuehow, N., 2757.
Paraf-Javal, 2722.
Parker, H., *see* J. Garner.
Parkes, A., 2658.
Parkin, W. and A. Williams, 2581, 2672.
Pasavant, S., *see* H. Reichenbach.
Paschke, F., 2899.
Paschke, F. and Safety Celluloid Co., 2596.
Paterno, E., 2751.
Paterno and Oglialoro, 2729.
Paterno and Pisati, 2739.
Pathe Freres, 2780.
Pauthonier, V., 2582, 2586.
Peck, J., 2890, 2900.
Perelzvich, V. and G. Rosenbuch, 2891.
Periere. G. and G. Guignard, 2677.
Perkin, A., *see* A. Green.
Perkins, 2949.
Persoz and Bloch, 2589.
Pervilhac, H. Co., *see* M. Ratignier.
Peters, H., 2796, 2805.
Peters, H. and H. Cullum, 2565.
Petit, A.. 2880.
Petterson, 2524.
Petterson. O., 2519.
Peyrusson, A., 2711.
Philip, J.. 2528, 2905.
Photochemie, G. m. b. H., 2789.
Pianko, M., 2814.
Pichon, H. and T. Truchelut, 2722.
Pictet, A., 2651.
Pictet, A. and P. Genequand, 2703.
Piequet, O. and P., 2517.
Pierron, P., *see* E. Cote.
Piest, C., 2503, 2678.
Pikos, P., 2909.
Pinay, *see* Les Fils Pinay.
Pisati, *see* Paterno.
van Pittius, C., 2902.
Plaissetty, A., 2857.
Platsch, M., 2909.
Plinatus, 2578.
Plinatus, W., 2901.
Pluddemann, W., *see* F. Auerbach.
Pohl, E., 2909.
Polowzow, 2757.
Polowzow, V., 2523.
du Pont de Nemours Powder Co., 2712, 2716, 2735.
Porter, M., 2724.
Portes.. and Ruyssen, 2906.
Prager, M., 2521.
Prandtl and Borinski, 2589.
Pregl, F., 2645.
Prost, P. and Les Fils Pinay jeune, 2608.
Prudhomme, 2589.
Pueschel, A., 2771.

Quartaroli, A., 2906.

Raabe, B., *see* P. Roeder.
Raabe, P., 2956.
Radcliffe, L., 2722.
Ragow, 2931.
Raison Sociale Siebert, 2810.
Rakusin, M., 2757.
Ramsey, *see* McTavish.
Ramsey, A., 2855.
Ramsey and Lewis, 2903.
Ramsey, W. and S. Young, 2524.
Raschig, E., 2715.
Raschig, F., 2669.
Rathman, W., *see* W. Herz.
Rathman, W., 2719.
Ratignier, M. and H. Pervilhac Co., 2866.
Raynaud, A., 2648.
Reboul, E., 2736.
Reeser, H., 2762, 2765, 2784, 2860.
Regnault, 2589.
Regnault, V., 2751.
Reichenbach, H., 2865.
Reichenbach, H. and S. Pasavant, 2865.
Reid, D., 2752.
Remmstedt, O., 2725.
Rex, 2722.

Rheinische Gummi u. Zelluloid Fabrik, 2712, 2713.
Rheinisch-Westfalische Sprengstoff Aktiengesellschaft, 2784.
Richardson, C. and C. Forrest, 2724.
Richmond, H., 2525.
Richter, J., 2765.
Riederer, H., see C. Baskerville.
Riegel, E., *see* C. Sanger.
Rimbach, E. and R. Wintgen, 2524.
Rinman, E., 2522.
Rivett, A. and N. Sidgwick, 2524.
Riviere, C., *see* L. Clement.
Riviere, C., 2748.
Robinoff, M., *see* C. Schwalbe.
Robinoff, M., 2503.
Robinson, J., 2724.
Roeder, P. and B. Raabe, 2835.
Roggenkaemper, 2805.
Rogow, 2931.
Roll, 2882.
Romer, 2739.
Rose, 2589.
Rosenbuch, G., *see* V. Perelzvich.
Rosenstiehl, 2589.
Ross, D., 2730.
Rossi, C., 2910.
Rost, A., 2784.
Roth, C., 2757.
Rothwell, *see* Thornton.
Rousseau, E., 2754.
Rouxeville, E., 2708.
Ruedorff, F., 2524.
Rupp, E., 2519, 2905.
Rutstein, L., *see* E. Worden.
Rutstein, Leo, 2987.
Ruyssen, *see* Portes.

Sabanejeff, 2740.
Sabatier, P. and A. Mailhe, 2519.
Safety Celluloid Co., *see* F. Paschke.
Safety Celluloid Co., 2584.
Saget and Suevern, 2818, 2830.
Salamon, M. and W. Seaber, 2690.
Salzbergwerk Neu Stassfurt, 2741, 2750, 2753.
Salzbergwerk Neu Stassfurt and Theilnehmer, 2751.
Sammet, F., 2824.
Sandell, Plates and Films Ltd. and W. Smalley, 2866.
Sanger, C., 2589.
Sanger, C. and E. Riegel, 2589.
Sanson, J., *see* Fauconnier, A.
Sansone, A., 2843.
Sapojnikoff, V., 2519.
Saruw, 2535.
Saxton, B., *see* J. Garner.
Schaefer, W., *see* H. Haberland.
Scala, 2906.
Schelenz, H., 2757.
Schenck, R., 2703.
Schidrowitz, P., 2909.
Schiff, 2589.
Schiff, R., 2735.
Schindler, A., 2504.
Schleimann, W., 2513, 2546, 2547.
Schloss, A., 2681.
Schlutting, 2816.
Schmerber, J., 2710.
Schmerber, J. and L. Morane, 2650, 2761.
Schmidt, O., G. Lutz and T. Eichler, 2716.
Schmidtz, A., 2728.
Schmitz, W., *see* A. Tschirch.
Schneeberger, L., 2822.
Schoenbein, 2659.
Schraube, C. and E. Laudien, 2706.
Schroder, H., 2516, 2517.
Schroeder, C., L. Levi and A. Lasche, 2887.
Schuepphaus, R., 2709.
Schuetzenberger, P., 2530, 2531, 2589, 2642, 2659.
Schuetzenberger, P. and L. Naudin, 2530.
Schultz, H., 2535.
Schwabe, C., 2539.
Schwalbe, 2540, 2590, 2822, 2947.
Schwalbe, C., 2503, 2562, 2924.
Schwalbe, C. and M. Robinoff, 2503.
Schwalbe, K., 2540.
Schwers, F., 2524.
Scopes, *see* Gowing-Scopes.
Scott, 2523.
Scott and Henderson, 2523.
Seaber, W., *see* M. Salamon.
Seaton-Snowden, F., *see* D. Young.
Seelig, E., 2708.
Seiler, E., *see* K. Hofmann.
Sendereus, J. and J. Aboulene, 2690.
Sertuerner, 2588.
Shipsey, K. and E. Werner, 2677.
Shrager, C. and R. Lance, 2956.
Sidgwick, M., 2528.
Sidgwick, N., *see* A. Rivett.
Sidgwick, N., *see* B. Wilsdon.
Sirk, H., *see* Skraup.
Skraup, 2510, 2655, 2927, 2929, 2933, 2946.
Skraup and Koenig, 2929.
Skraup, Z., 2509, 2535, 2604.
Skraup, E. Geinsperger, E. v. Kraffl-Lenz, F. Menter and H. Sirk, 2644.
Skraup, Z. and H. Hamburger, 2644.
Skraup, Z. and Koenig, 2509, 2535.
Skraup, Z. and R. Kremann, 2509.

Slater, C., *see* J. Ekeley.
Smalley, W., *see* Sandell Plates and Films Ltd.
Smith and Berl, 2944.
Smith, A. and K. Orton, 2538.
Smith, J. and W. Merckens, 2859.
Smith, W., *see* E. Berl.
Snowden, *see* Seaton-Snowden.
Snowden & Co., 2762, 2902.
Societe Anonyme des Celluloses Planchon, 2811.
Soc. Anon. des Etablissements Eycken et Leroy, 2518.
Societe Anonyme d'Etudes Electrochimiques, 2723.
Societe Anonyme D'Explosifs at de produits Chemiques, 2601. 2724.
Societe Anonyme des Usines des Moulins, 2517.
Societe Anonyme Le Camphre, *see* also Le Camphre.
Societe Anonyme Le Camphre, 2685, 2761, 2765.
Societe Anonyme L'Oyonnaxienne, 2588, 2716.
Societe Anonyme Nouvelle L'Oyonnithe, *see* also Societe L'Oyonnithe.
Soc. Anon. Nouvelle L'Oyonnithe, 2711, 2771, 2772.
Societe Anonyme par Acations "La Solvea," 2904.
Societe Ballaud et Cie, 2813.
Societe Chimique des Usines du Rhone, 2606, 2903.
Societe Civile des Pellicules Nouvelle pour Cinematographes, 2866.
Societe Debauge et Cie, 2747, 2796, 2852, 2855.
Societe des Manufactures N. Konchine, 2903.
Societe D'Exploitation des Brevets Dolter, 2687, 2853.
Soc. du Bec. Francais, 2725.
Societe Generale des Firms and C. Gonon, 2866.
Societe Generale des Tissue Biaises, 2882.
Societe Generale pour la fabr. des Matieres Plastiques, 2712.
Societe Industrielle de Celluloid de Paris, 2783.
Societe Industrielle de Mulhouse, 2787.
Societe Industrielle des Telephones, 2801.
Societe Leduc, Heitz et Cie, 2755, 2796, 2883.
Societe Neumann, Marx & Desvaux, 2716.
Societe L'Oyonnithe, *see* also Societe Anonyme Nouvelle L'Oyonnithe.
Societe L'Oyonnithe, 2527, 2587, 2685.
Societe Pages Camus et Cie, *see* L. Pages.
Societe Pages Camus et Cie, *see* also Pages Camus et Cie.
Soc. pour L'Industrie Chim. Bale, 2518.
Society of Chemical Industry, Basle, 2762.
Soederlund, O., 2909.
Sonstadt, E., 2524.
Sorger, C., 2692.
Sparre, F. and W. Masland, 2740.
Squire, P. and C. Caines, 2525.
Stavorinus, D., 2757.
Stein, A., 2541, 2542, 2637, 2640.
Steinkopf, W., 2703.
Steinkopf, W. and G. Kirchhoff, 2703.
Stephan, J., 2787.
Stephani, O., *see* P. Benrath.
Stevens, G., 2718, 2880.
Stevens, J., 2709, 2715.
Stevens, J. and M. Lefferts, 2865.
Stewart, F., 2504.
Sthamer, R., 2559.
Stiebel, A., 2824.
Stockhausen, C. and Traiser, 2724.
Stockhausen, J., 2724, 2750.
Strange, E., *see* A. Fernbach.
Strauss, D., 2517.
Stremayr, *see* Hardt-Stremayr.
Sudborough, J. and W. Thomas, 2921.
Suevern, *see* Saget.
Suida, W., 2897.
Sulzer, H., 2518, 2903.
Sulzer-Rieter, H., 2518.
Surcouf, P., 2724.
Swinne, R., see B. Walden.
Swinton, R., 2909.
Syniewski, V., 2646.

Tauss, 2503.
Taylor, A., *see* J. Hardcastle.
Tessler, A., 2900, 2956.
Thiele, 2931.
Thiele, E., 2817, 2931.
Thiele, J., 2534.
Theilnehmer, *see* Salzbergwerk.
Thieme, O., 2708.
Thole, *see* Dunstan.
Thomas, W., *see* J. Sudborough.
Thompson, 2871.
Thomson, E. and J. Callan, 2633, 2847.
Thompson, F., 2898.
Thornton, J., 2866, 2898.

Thornton and Rothwell, 2866.
Thorpe, 2589.
Thorpe, T., 2751.
Timmermans, 2726.
Timmermans, J., 2722.
Tollens, *see* Faber.
Tollens, *see* T. de Haas.
Tompkins, T., 2740.
Tompkins, H. and Clayton Aniline Co., 2729.
Tondl & Co., 2899.
Traiser, *see* Crefelder Seifenfabrik.
Traiser, *see* C. Stockhausen.
Transier, 2931, 2946.
Traquair, *see* Cross.
Traquair, 2641, 2647, 2893, 2895, 2927, 2939.
Truchelut, T., *see* H. Pinchon.
Tsakalotos, D., 2523.
Tschirch, A. and W. Schmitz, 2749.
Tyrer, 2757.
Tyrer, D., 2722.

v. Unruh, 2784.
von Unruh, M., 2519.
Urbaine, etc., *see* Cie Urbaine, etc.
Urbain, A., 2723.
Usher, F., 2524.
Utz, 2722.

Vahlkamp, E., 2805.
Valenta, 2548.
Valenta, E., 2857.
Van Lennep, D., 2730.
Veley, H., 2730, 2743, 2744, 2749.
Vender, V., 2690.
Vereinigte f. Chemische Industrie, Frankfurt, 2526.
Vereinigte f. Chemische Industrie in Mainz, 2578, 2579, 2580, 2903, 2904, 2957.
Vereinigte Glanzstoff Fabriken Akt.—Ges., 2621, 2627, 2631, 2681, 2762.
Vereinigte Kunstseidenfabriken, 2829.
Verley, A., 2725.
Vieille, 2544, 2618.
Vieweg, 2656, 2824, 2854, 2885.
Vignon, 2947.
Vignon, L., 2544, 2559, 2567.
Vignon and Gerin, 2930, 2946.
Vignon, L., and E. Guerin, 2535, 2548, 2559.
Villani, F., 2521.
Viscose Development Co., 2807.
Viscose Development Co. and J. Morford, 2881.
de Visser, L., 2524.
Vogelsohn, C., *see* P. Askenasy.
Voight, J., 2742.

Waage, *see* Guldberg.
Wagner, 2835.
Wagner, A., 2843.
Wagner, H., *see* J. Heilman.
Waite, C., 2860, 2681.
Walden, 2757.
Swinne, 2735.
Walden, P. and R.
Walker, W., *see* H. Mork.
Walker, W.. 2518, 2540, 2544, 2559, 2700, 2746, 2761, 2796, 2818, 2866.
Wall, E. J., 2873.
Walters, 2789.
Walther, T., 2519.
von Walther, F., 2909.
Wasiljeff, *see* Menschutkin.
Watt, A., 2736.
Weber, C., 2534, 2548.
Weber, C. and C. Cross, 2557, 2634, 2639, 2736, 2762.
Weeber, R., 2900.
Wegscheider, R. and F. Zmerzlikar, 2689.
Weintraub, *see* Lunge.
Weintraub, 2544.
Weise, J., 2518.
Weiss, J., 2756, 2757.
Wendriner, W., 2956.
Wenzel, F., 2921.
Werner, E., *see* K. Shipsey.
Wichern, H., 2757.
Wild, E., 2757.
Wild, R., 2890.
Will, 2945.
Williams, 2589.
Williams, A., *see* W. Parkin.
Williamson, A., 2589.
Williamson, R., 2589.
Willstaetter, R. and L. Zechmeister, 2898, 2614.
Willstaetter, W., 2508.
Wilsdon, B. and M. Sidgwick, 2528, 2909.
Wintgen, R., *see* E. Rimbach.
Withrow, J., *see* E. French.
Wohl, 2557, 2928.
Wohl, A., 2527, 2575, 2587, 2656, 2685, 2693, 2718, 2762.
Woodbridge, R., 2623, 2638.
Woodcock, R., *see* C. Kingzett.
Woodhouse, H., *see* W. Denham.
Worden, Dean S., 2975.
Worden, E,. 2524, 2540, 2617, 2634, 2642, 2888.
Worden, E. and L. Rutstein, 2617, 2739.
Wotherspoon, W., 2525, 2893.

Young, D., J. Minuto and F. Seaton-Snowden, 2608.
Young, S., *see* W. Ramsey.
Young, S., 2528, 2722.

Zanninovich - Tessarin, 2519.
Zapon, Lack, Ges., 2956.

Zechmeister, L., *see* R. Willstaetter.
Zelensky, M., 2854.
Zellstoff-fabrik Waldhof, 2504.
Zemplen, G., 2513.
Zimmer, A., 2732, 2804.
Zmerzlikar, F., *see* R. Wegscheider.
Zuehl, E., 2651, 2682, 2683, 2710, 2712, 2713, 2715, 2716, 2760, 2860.
Zuehl and Eisenmann, 2682, 2710, 2712, 2713, 2760.
Zulkowsky, K., 2645.
Zwick, H., 2853.

INDEX OF SUBJECTS

Prepared by

LEO RUTSTEIN

Absorbent cotton, see Cotton, absorbent.
Acacia 2785
—, substitute for, acetated starch as 2896
Acetaldehyde, *see also* Aldehyde.
—, ... 2521, 2527, 2673
—, manufacture acetic acid from 2907
—, oxidation of, to acetic acid 2522
Acetaldol 2712, 2716
Acetals, cyclic 2711
Acetamide 2697
—, plastic of cellulose acetate and 2764
Acet-*o*-amidotoluene, *see o*-Acettoluide.
Acetanilid 2524, 2700, 2709, 2826
—, dissolving ethyl cellulose by 2506
—, formation 2917
Acetanilids, substituted 2709, 2767
Acetate bronzing liquids 2801
Acetate collodion 2888
Acetate lacquer 2789
—, coating gelatin with 2813
—, coating viscose with 2813
—, pyridine in 2702
Acetate silk, *see* Filaments, artificial, cellulose acetate.
Acetated castor oil, *see* Castor oil, acetated.
Acetated cellulose, *see* Cellulose, acetated.
Acetated pyrogallol 2692
Acetated starch, *see* Starch, acetated.
Acetated starch, see Starch, acetated.
Acetated turpentine, *see* Turpentine, acetated.
Acetation, *see* also Esterification.
—, catalysts in 2540, 2541
—, comparison with nitration 2551
—, controlling 2558
—, details of 2535, 2567, 2568, 2569, 2570, 2571
—, gelatinization in 2569
—, influence catalyzers upon 2538
—, maximum 2537
—, modifying 2558
—, raw materials for 2501
—, speed of 2554
—, sulfuric acid in, role of 2569
—, superficial 2843
—, theory of 2550
Acetbenzenesulfoamid 2714

Acetdiphenylamine 2716
Acetic acid 2520
—, acceleration of acetation in..... 2539
—, acidity in, determining..... 2911
—, analysis of acetic anhydride and..... 2910
—, analysis, permanganate method..... 2910
—, anhydrous, *see* Acetic anhydride.
—, binary solution equilibrium..... 2525
—, cellulose acetate insoluble in..... 2607
—, cellulose acetate soluble in..... 2681
—, congealing point of..... 2524
—, —, determining 2908
—, constants of..... 2523
—, crystallization temperature of..... 2524
—, decolorizing 2523
—, dehydration of..... 2523
—, density, determining.....2523, 2524, 2916
—, determining in cellobiose acetates..... 2511
—, dissolving cellulose acetate in.....2576, 2892
—, dissolving cellulose esters with.....2856, 2857
—, dissolving ethyl cellulose by..... 2506
—, distillation, rate of..... 2525
—, estimation acetic anhydride in..... 2909
—, estimation by titration..... 2910
—, estimation of formic acid in, Delahye method..... 2909
—, —, Pikos method..... 2909
—, fusion, heat of..... 2525
—, glacial, *see also* Acetic acid, concentrated.
—, —, analysis of 2907
—, —, cellulose acetate and casein plastic with..... 2766
—, —, determining strength of..... 2524
—, —, properties 2569
—, —, strength of 2524
—, heat of fusion of..... 2525
—, heat of liquefaction of..... 2525
—, hydrates of 2525
—, hydration, rate of..... 2909
—, hydrolysis 2905
—, liquefaction, heat of..... 2525
—, manufacture 2955
—, —, catalysts for 2907
—, —, Cohoe process 2903
—, —, Deiss process 2909
—, —, electrolytic 2907
—, —, French and Withrow process..... 2907
—, —, from acetaldehyde 2907
—, —, from acetylene 2522
—, —, from coffee husks.....2521, 2907
—, —, from ethylene 2522
—, —, from sodium acetate..... 2908
—, —, from turpentine 2519
—, —, Guignard process 2909
—, —, Hoesch process 2909
—, —, Konsortium process 2909
—, —, Meunier process 2909
—, —, Pohl process 2909

Acetic acid, manufacture, Soederlund process 2909
—, —, Swinton process 2909
—, —, von Walther process 2909
—, melting point of 2524
—, miscibility of with solvents 2524
—, molecular refraction of 2914
—, occurrence 2520
—, purification of 2522, 2523
—, reactive esterification velocity of 2618
—, recovery from acetating bath 2612
—, refraction of 2914
—, resistance of sheet steel enamels to 2523
—, sawdust for manufacture of 2521
—, silicon tetrachloride in manufacture of 2521
—, substituted, acetation with 2600
—, uses of 2526
—, viscosity curves of 2525
—, water in, determination of 2907, 2908
Acetic anhydride 2526
—, acetating with vapours of 2606
—, acidity of, determining 2911
—, action of, on benzylideneanthranilic acids 2909
—, —, on cotton 2528
—, analysis 2910
—, —, acetic acid and 2910
—, —, aniline method 2917
—, —, gravimetric 2910
—, —, Menschutkin method 2917
—, —, refractometric 2914, 2915
—, commercial, properties 2568
—, density determination 2916
—, detection 2908, 2909
—, duty on 2528
—, estimating small amounts of 2909
—, estimation acetic acid in 2909
—, hydration, rate of 2528
—, hydrolysis of 2528
—, manufacture of 2527, 2588, 2613, 2912, 2955
—, —, Beatty process 2909
—, —, Behren process 2907
—, —, from acetaldehyde and chlorous anhydride 2527
—, —, from sulfuryl chloride 2527
—, —, Goldschmidt process 2526
—, —, sulfuryl chloride process 2909
—, properties of 2527, 2528
—, purifying 2527
—, recovery of 2611
—, —, from acetating bath 2589, 2612, 2613
—, refraction of 2914
—, strength of 2568
—, titration, calculation of 2913
Acetic collodion 2856
Acetic ether, *see* Ethyl acetate.
Acetic lacquers 2525
Acetic oxide, *see* Acetic anhydride.
Acetic-propionic anhydride, manufacture 2907

Acetin, *see* Glyceryl triacetate, Triacetin.
Acetin-diformin 2690
Acetin-formin 2690
Acetin-monoformin 2690
Acetoacetic ester, *see* Ethyl acetoacetate.
Acetocellulose sulfuric acid esters, *see* Cellulose acetate sulfuric acid esters.
Acetochlorgalactose 2509
Acetochlorglucose 2509
Acetochlorhydrin 2689, 2704, 2715, 2783, 2785, 2861
—, cellulose acetate plastic containing..... 2765
Acetochlorhydrin diacetate 2689
Acetochlorhydrose 2713, 2774
Acetochlorlactose 2509
Acetochlorobiose 2509
Acetodichlorhydrin 2630, 2704, 2737, 2826
Acetol, *see* Acetyl methyl alcohol.
Acetolysis 2502, 2509, 2511, 2515, 2538, 2927
Acetone, acetation in.....2539, 2677, 2678
—, catalysis of 2717
—, cellulose benzoate solvent..... 2657
—, dissolving ethylcellulose by..... 2506
—, hydrocellulose aceto-nitrate solvent..... 2649
—, hydrogenation of 2677
—, increasing solubility cellulose acetate by..... 2955
—, manufacture of 2528, 2674
—, manufacture cellulose acetate insoluble in..... 2534
—, manufacture cellulose acetate soluble in.....2561, 2579, 2904
—, manufacture diacetone alcohol from..... 2717
—, manufacture from starch..... 2674
—, manufacture from wool..... 2677
—, miscibility of acetic acid with..... 2524
—, properties of 2675
—, purification of 2677
—, purification wood cellulose by..... 2504
—, solubility 2675
—, solubility cellulose propionate in..... 2638
—, starch acetate solvent..... 2935
—, substitute for 2678
Acetone oil, heavy..... 2677
—, light 2677, 2745, 2794, 2808
—, manufacture cellulose acetate soluble in..... 2574
—, preserving wood with..... 2678
Acetophenone 2524, 2679, 2709
—, chlorinated 2679, 2728
—, plastic of cellulose acetate and..... 2764
Acetosulfonic esters 2550
Acet-*p*-phenetidin 2709
o-Acetphenetidin 2709
p-Acetphenetidin 2709
Acet-*p*-toluenesulfamid 2714
o-Acettoluide 2709
p-Acettoluide 2709
Acetxylid 2715
Acetylacetone 2528
Acetyl-albumin 2809

Acetylamylaniline 2700
Acetyl aniline 2630
Acetylated cellulose, *see* Cellulose acetate.
Acetylated glucose 2615
Acetylated lactose 2616
Acetylated levulose 2616
Acetylated saccharose 2616
Acetylated starch, *see* Starch acetate.
Acetylated triglucose 2532
Acetylation, *see* Acetation.
Acetylbenzidine 2711
Acetylbenzoyl-*o*-toluidine 2826
Acetylbenzyl-*o*-toluidine 2694
Acetylbutylaniline 2700
Acetylcellobiose 2509
Acetylcellulose, *see* Cellulose acetate.
Acetyl chloride....2549, 2556, 2557, 2560, 2562, 2563, 2643, 2649
—, acetylation with 2534, 2928
—, chlorination 2754
—, manufacture of 2526, 2527
Acetylchloromaltose 2645
N-Acetyl compounds, analysis of..... 2921
Acetyldianisidine 2711
Acetyldichlorbenzidine 2711
Acetyldiglucose 2713
Acetyldiphenylamine 2701, 2705
Acetylene, manufacture of acetic acid from..... 2527
—, manufacture of acetic anhydride from..... 2527
—, manufacture of dichlorethylene from..... 2727
Acetylene, chlorides of.....2719, 2901
—, chlorination of 2741, 2742
Acetylenedichloride 2725, 2741
—, dissolving ethyl cellulose by..... 2506
Acetylene tetrabromide, *see* Tetrabromethane.
Acetylene tetrachloride, *see* Tetrachlorethane.
Acetylethylaniline 2664, 2686, 2700
Acetyl glucoses, *see* Glucose acetates.
Acetylheptachlormaltose 2615
Acetylhydrocellulose, *see* Hydrocellulose acetate.
Acetylidine tetrachloride 2661
Acetyllactose 2713
Acetyllevulose 2713
Acetyl methyl alcohol..... 2679
Acetylmethylaniline 2700, 2701, 2958
Acetyl methylated cellulose..... 2508
Acetylnaphthylamine 2705
Acetyl nitrate..... 2651
Acetylnitrocellulose, manufacture artificial rubber with..... 2884
Acetyl oxide, *see* Acetic anhydride.
Acetyloxycellulose 2714
Acetyl palmitic esters..... 2828
Acetylphenylnaphthylamine 2701
Acetylphenyltolylamine 2701, 2705
Acetylpropylaniline 2700
Acetyl-saccharose,, *see* Saccharose acetate.
Acetylsalicylate 2688

Acetylsulfuric acid, *see* Sulfacetic acid.
sym-Acetyltetrachloraniline 2709
Acetyltolidine 2711
Acetyltolylamine 2701
Acetyltolylxylylamine 2701
Acetyltrichlor-*o*-phenylenediamine 2710
Acid cellulose, preparation of 2538
Acid pyridine sulfate 2637
Acid radicals, determining 2921
Acids, cellulose acetate solvents 2680
—, hydrating cellulose esters with 2576
Aconitic acid, glycol ester of 2688
Acridine 2702
Adhesive, acetated starch as 2896
—, manufacture cellulose acetate containing 2566
—, starch acetate as 2897
Adhesives, cellulose acetate 2900
—, starch acetate for 2501
Aeronautics, *see* also Aviation, Aircraft, Balloon.
—, cellulose acetate in 2886
Aeroplane fabric, coating with cellulose acetate 2801
Aeroplane, lacquer for, cellulose acetate 2956
—, manufacture, cellulose acetate in 2882
Aeroplane window, cellulose acetate sheet for 2879
Aeroplane wings, waterproofing 2806
Agglutinants, *see* Adhesives.
Air-craft, *see also* Aeronautics, Balloon, Aviation.
Air-craft, lacquer for, cellulose acetate 2956
—, manufacture, cellulose acetate in 2882
—, windows in, cellulose acetate for 2784
Air-ship, *see* Air-craft.
Ajacol 2670
Albumen 2785
—, formylated 2716
—, insulating wire with 2849
—, plastic of cellulose acetate and 2774
Albumin 2809
—, acetyl 2809
—, plastic of cellulose acetate and 2667
Albumins, *see also* Casein and Caseinates.
—, plastic of cellulose acetate and 2773
"Alco Deo" 2717
Alcohol, burning, increasing speed of 2891
—, —, speed of, modifying by cellulose acetate 2892
—, —, —, modifying by cellulose esters 2892
—, cellulose acetate soluble in benzyl alcohol and 2583
—, cellulose formate precipitant 2629
Alcohol cubes 2890
Alcohol, ethyl, manufacture from sawdust 2521
—, gelatinizing 2891, 2982
—, heptavalent, heptacetyl 2929
—, hydrating cellulose esters with 2582
—, increasing porosity of cellulose acetate with 2838
—, increasing solubility cellulose acetate by 2955
—, manufacture cellulose acetate insoluble in 2561
—, manufacture cellulose acetates soluble in 2562

Alcohol, precipitating cellulose acetate by.....2557, 2563, 2763
—, recovery of acetic anhydride by means of..... 2613
—, solidified, cellulose acetate as..... 2890
—, solidifying, Bayer process..... 2891
—, —, cellulose acetate for..... 2890
—, —, Denayrouze process 2891
—, —, le Fortier process..... 2891
—, —, Perelzvich process 2891
—, —, Wild process 2890
—, solidifying with cellulose acetate..... 2891
—, solidifying with cellulose nitrate..... 2891
—, solubility of cellulose acetate in..... 2562
—, solvent of pentachlorethane and 2762
—, travelers 2890
Alcohols, high, manufacture from starch..... 2674
—, miscibility of acetic acid with..... 2524
Aldehyde, *see* Formaldehyde, Acetaldehyde, etc.
—, acetylation of 2931
—, manufacture from trichloromercuriacetaldehyde 2527
—, oxidation of, to acetic acid..... 2522
Aldehydes, cellulose acetate solvents of..... 2672
—, condensing with phenols..... 2772
—, conversion of into diacetates..... 2538
—, sthenosage, by 2834
Aldols 2716
Algol 2612, 2628
—, dyeing cellulose acetate with..... 2841
Algol red B.....2841, 2842
Alizarin assistant 2587
Alkali, action of, on cotton..... 2503
Alkali cellulose, solubility in thiocyanates..... 2628
Alkaloids 2889
Alkylamine sulfates 2595
Alkylation, *see* Cellulose.
Alkylation (of Cellulose)..... 2897
Alkyl carbonates 2715
Alkyl citrates 2715
Alkyloxyphenyl compounds 2714
Alligator, imitating hide of..... 2808
Allyl alcohol 2617
p-Allylphenylmethyl ester, *see* Anethol.
Alum, toughening gelatin with..... 2765
Aluminum acetate 2890
—, (basic) 2806
Aluminum amalgam 2723, 2754
Aluminum chloride 2723, 2735
Aluminum oleate 2809
Aluminum oxide 2957
Aluminum palmitate 2809
Aluminum ricinoleate 2711
Aluminum stearate 2809
Amber oil 2704, 2893
Amides, plastics of cellulose acetate and..... 2764
Amidobenzene, *see* Aniline.
p-Amidophenetol 2709
Amidophenol 2668

Amido-phenols 2593, 2823
m-Amidosulfbenzoic acid 2714
o-Amidosulfbenzoic acid 2714
p-Amidosulfbenzoic acid 2714
Amidotoluene, *see* Toluidine.
Amines, aromatic, hydrating cellulose esters with..... 2579
Aminoazobenzene, impregnating cellulose acetate with..... 2837
Aminophenol, plastic of cellulose acetate and..... 2763
p-Aminophenol, diazotization of..... 2839
—, impregnating cellulose acetate with..... 2837
Aminosulfonic acid 2840
Ammonia, neutralizing catalysts with..... 2579
—, preparation of 2518
Ammonium acetate 2592, 2787
Ammonium bichromate, dissolving cellulose formate with.... 2632
Ammonium bisulfate, acetating cellulose with..... 2587
Ammonium carbonate, neutralizing with..... 2566
Ammonium chloride 2597, 2890
—, acetation with 2538
—, acetylating cellulose with..... 2582
—, decreasing inflammability of celluloid with..... 2901
—, reducing inflammability with..... 2610
Ammonium formate 2518
Ammonium metantimonate 2793
Ammonium metavanadate 2793
Ammonium nitrate 2593, 2955, 2957
—, acetylating cellulose with..... 2582
—, dissolving cellulose formate with..... 2632
Ammonium paratungstate 2793
Ammonium persulfate.....2951, 2952, 2953, 2954
—, catalyzer 2940
Ammonium sulfate 2541, 2635
—, acetation with 2538
Ammonium sulfocyanide, cellulose acetate solvent.....2622, 2665
—, dissolving cellulose acetate by..... 2800
Ammonium thiocyanate, *see* Ammonium sulfocyanide.
Amylacetanilid 2709
Amyl acetate....2529, 2687, 2707, 2776, 2824, 2853, 2865, 2882, 2885, 2898, 2956
—, cellulose acetate gelatinizer..... 2665
—, cellulose formate precipitant.....2629, 2632
—, cellulose sulfonate solvent..... 2654
—, dissolving ethyl cellulose with..... 2506
—, hydrocellulose aceto-nitrate solvent..... 2649
—, insolubility hydrated cellulose acetate in..... 2575
—, manufacture cellulose acetate insoluble in.....2534, 2561
—, miscibility of acetic acid with..... 2524
—, solubility cellulose propionate in..... 2638
Amyl alcohol, *see also* Fusel oil, refined.
—, ...2746, 2805, 2885, 2924
—, cellulose acetate solvent..... 2665
—, combining nitroacetylcellulose with..... 2884
—, extraction of maize with..... 2716
—, increasing solubility cellulose acetate by..... 2955
—, insolubility hydrated cellulose acetate in..... 2575
—, miscibility acetic acid with..... 2524

Amyl alcohol, solubility cellulose propionate in..... 2638
Amyl anthranilate 2692
Amyl benzoate 2692
Amyl butyrate 2697
—, dissolving ethyl cellulose by..... 2506
Amyl carbanilate 2715
Amyl chloride 2805
Amyl chlorstearate 2711, 2880
Amyl ether 2805
Amyl formate 2633, 2687
—, cellulose formate precipitant..... 2629
Amyl lactate 2673, 2688, 2696
—, plastic cellulose benzoate and..... 2658
Amyl myristate 2688
Amyl naphthoxylacetate 2713
Amyl nitrate 2688
Amyl nitrite 2688
Amyl oxide, *see* Amyl ether.
Amyl palmitate 2688
Amyl phthalate 2715
Amyl silicate 2688, 2793, 2805
Amyl stearate 2688
Amyl succinate 2715
Amyl valerianate 2697
Amylene oxide 2678
Amylidenedimethyl ether 2701, 2705
Amylidenediethyl ether 2701, 2705
Amyloid 2514
Anethol 2860
—, cellulose acetate solvent..... 2666
Anhydroformaldehydeaniline 2700
Anhydroformaldehydeaniline resinate 2766
Anilids 2700
—, dissolving ethyl cellulose with..... 2506
—, substituted, cellulose acetate softeners..... 2700
Aniline.....2580, 2593, 2672, 2691, 2698, 2699, 2784, 2778, 2823
—, analysis acetic anhydride with..... 2917
—, cellulose benzoate solvent..... 2658
—, dissolving ethyl cellulose by..... 2506
—, hydrating cellulose acetate with..... 2580
—, hydrating cellulose esters with..... 2582
—, hydrating with 2579
—, hydrolyzing cellulose acetate with..... 2578
—, increasing porosity of cellulose acetate with..... 2838
—, manufacture of cellulose acetate soluble in.....2546, 2565
—, plastic of cellulose acetate and..... 2763
Aniline acetate 2691
Aniline bisulfate 2595
Aniline black 2786, 2788
—, dyeing cellulose acetate with..... 2839
Aniline oil, *see* Aniline.
Aniline resinate 2694
—, plastic of shellac and..... 2766
Aniline sulfate 2595, 2636
Aniline yellow, dyeing cellulose acetate with..... 2839
Anisic aldehyde 2704
Anisol, *see* Methyl-phenyl ether.

Anthranilic acid, esters of..... 2692
—, glycol ester of..... 2688
Antifouling lacquers 2731
Antifouling varnishes 2731
Antimonates 2793
Antimonous chloride, dissolving cellulose acetate by..... 2800
Antimony, salts of, antifouling paint containing..... 2731
Antimony pentachloride 2739, 2741
Antimony trichloride, *see* Antimonous chloride.
—, ... 2597, 2739
—, cellulose acetate solvent..... 2665
Antique leather, *see* Leather, antique.
Ants, formic acid in..... 2516
Apiol, cellulose acetate solvent..... 2666
Anise camphor, *see* Anethol.
Apple oil, *see* Amyl valerianate.
Apyroid 2784, 2789
Arabite 2693
Arabitol pentacetate 2693
Argentic, *see* Silver.
Argonite 2789
Arms, artificial, manufacture cellulose acetate..... 2900
Aromatic amines, *see* Amines, aromatic.
Aromatic sulfonic acids..... 2590
Arsenic, anti-fouling paint containing..... 2772
Artificial bristles, *see* Bristles, artificial.
Artificial filaments, *see* Filaments, artificial.
Artificial foil, *see* Foil, artificial.
Artificial hair, *see* Hair, artificial.
Artificial leather, *see* Leather, artificial.
Artificial rubber, *see* Rubber, artificial.
Artificial silk, *see* Silk, artificial; Filaments, artificial.
Artificial sponge, *see* Sponge, artificial.
Asbestos, cellulose acetate and..... 2770
—, impregnating with cellulose acetate..... 2813
—, platinized 2523
—, plastic of cellulose acetate and..... 2768
Ash, determining, in cellulose..... 2502
Aspartic acid, glycol ester of..... 2688
Aubepine, see Anisic aldehyde.
Auramine 2797, 2810, 2838, 2860
Aurine 2797, 2810
Ausperite 2801
Automobile, wind shields for, cellulose acetate..... 2879
Automobile shields 2871
Automobiles, windows, cellulose acetate for..... 2784
Aviation, *see also* Aeronautics, Air-craft, Balloon.
Avolin 2690
Azochromin, dyeing cellulose acetate with..... 2839
Azo Turkey Red, dyeing cellulose acetate with..... 2839

Bakelite 2787
Balances, lacquering, cellulose acetate for..... 2797
Balata, resins, cellulose acetate and..... 2772
Ballistite 2846

Balloon, *see also* Air-craft, Aviation, Aeronautics.
—, lacquering, cellulose acetate for.....2882, 2956
—, manufacture, cellulose acetate in..... 2882
—, varnishing, cellulose acetate for..... 2882
Balloon fabric, manufacture of..... 2882
Balloons, waterproofing fabrics for, cellulose acetate for..... 2813
—, webs of, cellulose acetate for coating..... 2784
Balls, billiard, coating..... 2799
—, golf, coating 2799
Balsam, *see* Copaiba.
Balsam of Peru, *see* Peru Balsam.
Balsam of tolu, *see* Tolu balsam.
Banana oil 2801
Bands, cellulose acetate, hydrating..... 2578
—, cellulose aceto-nitrate 2649
Baras camphor, *see* Borneol.
Barium acetate 2674
Barium benzenesulfonate 2921
Barium calcium acetate..... 2674
Barium caprylate 2888
Barium carbonate 2805
Barium chloride, reducing inflammability with..... 2610
Barium formate 2619
Barium hydroxide 2910
Barium phenolsulfonate 2590
Barium sulfate 2801, 2805
—, white enamels containing..... 2798
Barium sulfide 2798
Barnacles, paints poisonous to..... 2773
Basic nigrosines, see Nigrosines, basic.
Battery plates, cellulose butyrate for..... 2639
Baykogarne, *see* Bayko yarn.
Bayko yarn 2824, 2825
—, properties of 2827, 2828
Bed linings, waterproofing, cellulose acetate for..... 2902
Bedsteads, metallic, coating..... 2798
Beeswax, dissolving ethyl cellulose by..... 2506
Belting, cementing, cellulose acetate for..... 2901
Benzal chloride 2711
Benzaldehyde 2566, 2708
Benzanilid 2709
Benzene 2755
—, acetation in 2539
—, acetation in presence of..... 2565
—, cellulose acetate lacquers containing..... 2748, 2749
—, cellulose acetate soluble in alcohol and..... 2583
—, chlorination 2757
—, commercial, composition of..... 2757
—, commercial grades 2756
—, deodorizing 2757
—, dissolving ethyl cellulose by..... 2506
—, halogenized 2734
—, increasing solubility of cellulose acetate by..... 2955
—, inflammability, reducing..... 2757
—, inhibiting acetation with..... 2606
—, insolubility hydrated cellulose acetate in..... 2575

Benzene, manufacture cellulose acetate soluble in alcohol and 2582
—, manufacture in Russia 2757
—, precipitating cellulose acetate by 2820
—, properties 2757
—, recovery of acetic anhydride by means of 2613
—, recovery, plant for 2757
—, solubility cellulose propionate in 2638
—, solubility in water 2757
Benzene bromides 2715
Benzene chlorides 2715
Benzene nitrobromides 2715
Benzene nitrochlorides 2715
Benzenesulfamid 2714
Benzenesulfanilide 2714
Benzenesulfinic acid 2594, 2598, 2650
Benzenesulfoamid 2767
Benzenesulfanilid 2714
Benzenesulfodimethylamin 2714
Benzenesulfodiphenylamin 2714
Benzenesulfoethylamid 2714
Benzenesulfoethylanilid 2714
Benzenesulfo-methylanilid 2714
Benzene sulfonamid 2704
Benzenesulfo-*a*-naphthylamine 2714
Benzenesulfo-*b*-naphthylamine 2714
Benzenesulfonic acid 2605, 2921
Benzenesulfo-*o*-chloranilid 2714
Benzenesulfo-*o*-phenetidin 2714
Benzenesulfo-*p*-phenetidin 2714
Benzenesulfo-*o*-toluid 2714
Benzenyltrichloramidine 2713
Benzhydrol 2669
Benzhydrols 2768
Benzicin 2715
Benzidin 2702, 2711
—, diazotization of 2839
—, impregnating cellulose acetate with 2837
Benzine 2755
—, 62° 2756
—, acetylation in presence of 2756
—, cellulose acetate soluble in alcohol and 2583
—, decolorizing 2757
—, degreasing cotton with 2503
—, deodorizing 2757
—, insolubility hydrated cellulose acetate in 2575
—, miscibility 2756
—, precipitation of cellulose acetate in 2563
—, purifying 2757
—, solubility cellulose propionate in 2638
—, testing 2757
—, varnish makers, testing 2757
Benzinoform 2721
Benzinum 2721
Benzoale 2658
Benzoic acid 2774
—, esters of 2692

Benzoic acid, glycerol esters of.....2691, 2715
Benzoic anhydride 2641, 2658, 2715
—, hydration of, rate..... 2909
Benzoic esters 2774
Benzoic ether, *see* Ethyl benzoate.
Benzoin 2709, 2888, 2893
Benzol, *see* Benzene.
Benzolacetone, action acetic anhydride on..... 2513
Benzonaphthol 2693, 2715, 2771
Benzophenone 2524, 2679, 2709, 2728
Benzosol, *see* Benzoylguaiacol.
Benzoylation, *see* Cellulose, benzoylation.
Benzoylbenzenesulfamid 2714
Benzoyl chloride 2641, 2654, 2655, 2656, 2711
Benzoylguaiacol 2715
Benzoylnaphthylamine 2705
Benzoyltoluenesulfamid 2714
Benzum 2721
Benzyl 2709
Benzyl acetate 2661, 2685, 2690, 2691, 2708
Benzylacetylpentachloraniline 2709
s-Benzylacetyltetrachloranilid 2713
Benzyl alcohol 2690, 2728, 2768
—, cellulose acetate soluble in alcohol and..... 2583
—, cellulose acetate solvent..... 2665
Benzylaminobenzyl alcohol 2708
Benzyl benzoate 2629, 2691, 2692, 2704, 2708
Benzylbenzoyltetrachloranilid 2713
Benzylchloride 2711, 2769
—, cellulose acetate plastic with..... 2771
Benzyl cinnamate 2692, 2708
Benzyl compounds 2714
Benzyldihydrocarbon 2766
Benzyldihydrocarvone 2679, 2760
Benzyldihydropulegone 2630, 2679, 2766
Benzyldihydroxybenzene ethers 2671
Benzylethenyltrichloramidine 2713
Benzylethyl ether 2671, 2708
Benzylideneacetoacetic ester 2694, 2709, 2826
Benzylidene acetone 2709
Benzylideneanthranilic acids 2909
Benzylidine diacetate 2712, 2713
Benzylidene diaceticester 2708
Benzylidine diacetoacetate 2713
Benzylidine monoacetoacetate 2713
Benzyl-magnesium halogen 2679
Benzylmethyl ether 2671, 2708, 2768
Benzylnaphthalin 2712
a-Benzylnaphthalin 2712
b-Benzylnaphthalin 2712
Benzyl nitrochloride 2715
Benzyl oxanilate 2683, 2712
Benzylphenyl ether 2671
Benzyl quinol 2671
Benzyl salicylate 2692
Bergamot oil 2689

Betol 2715
Bichromates, dissolving cellulose formates with..... 2632
Billiard balls, coating..... 2799
Biose, *see* Cellobiose.
Biplane wings, *see* Wings, biplane.
Birch, acetating wood of..... 2568
Bismark brown 2797, 2842, 2888
—, dyeing cellulose acetate with..... 2839
Bismuth oxychloride 2824
Bismuth subchloride 2824
Bismuth subnitrate 2824
Bitumen, solvent, carbon tetrachloride for..... 2724
Black lacquers, cellulose acetate..... 2799
Blanc fixe 2786
Blasting gelatine 2846
Bleaching, cellulose acetate..... 2611
Bleaching cotton, *see* Cotton, bleaching.
Bleaching, electrolytic 2611
Block printing, *see* Printing.
Book-binding, cellulose acetate for..... 2829
Book covers, manufacture, cellulose acetate for..... 2902
Boots, artificial, manufacture, cellulose acetate for..... 2900
Borates, fireproofing with..... 2813
Borax 2642
—, decreasing inflammability of cellulose acetate by..... 2608
Boric acid, combing cellulose acetate with..... 2902
Borneo camphor, *see* Borneol.
Borneol 2707
Borneol, cellulose acetate, plastic with..... 2766
iso-Borneol, cellulose acetate plastic with..... 2766
Bornyl acetate, *see also* Isobornyl acetate.
Bornyl alcohol, *see* Borneol.
Boroid 2789
Boron compounds, aromatic 2768
Bottles, capping, cellulose acetate for..... 2881
Bottles, sealing, *see* Bottles, capping.
Braid, stiffening, cellulose acetate for..... 2815
Brass, imitating by lacquer..... 2797
Bristles, artificial, manufacture with cellulose acetate..... 2815
British gum 2785
Bromacetanilide 2709
Bromacetanilid 2709
p-Brombenzoyl chloride 2544
Bromides, dissolving cellulose formate with..... 2632
Bromine, esterifying hydrocellulose in presence of..... 2565
Bromine, manufacture oxycellulose with..... 2567
Bromine chloride, esterizing with..... 2565
—, manufacture cellulose formate with..... 2625
Bronze, darkening, preventing..... 2803
—, metallizing fabrics with 2813
—, oxidation of, preventing..... 2803
—, printing of, cellulose acetate for..... 2788
Bronze lacquer 2804
Bronze paints, cellulose butyrate for..... 2639
Bronzes, coating yarn with, cellulose acetate for..... 2825
—, fixation on textiles, cellulose acetate for..... 2787

Bronzes, printing with cellulose acetate and..... 2829
Bronzing liquid, cellulose acetate, Doerflinger formula..... 2801
—, cellulose nitrate 2801
Bronzing liquids 2792
—, adhesion of, increasing..... 2803
—, cellulose acetate 2801
—, —, acidity in, overcoming..... 2802
—, —, manufacture of 2801, 2802
—, cellulose butyrate for..... 2639
—, estimate of cellulose acetate in..... 2923
Brush lacquer, cellulose acetate..... 2791, 2795
Brush lacquers 2792
Brutto formula 2933
"Bubbles" (in films), testing for..... 2874
Buckles, lacquering, cellulose acetate for..... 2798
Buff split, *see* Skins.
Burnt umber 2888
Bushings, manufacture cellulose acetate for..... 2851
Butylacetanilid 2709
Butyl acetate 2529, 2824
n-Butyl acetate 2687
Butyl acetate, dissolving ethyl cellulose with..... 2506
Butyl alcohol, miscibility of acetic acid with..... 2506
Butyl anthranilate 2692
Butyl benzoate 2692, 2697
Butyl carbanilate 2715
Butyl chloral hydrate..... 2672, 2710
Butyl phthalate 2715
Butyl silicate 2793
Butyl succinate 2715
Butylene glycol 2666
Butylene glycol diacetate..... 2688
Butyric acid 2639, 2682
Butyric acid, hydration, rate of..... 2909
Butyric anhydride 2640
—, hydration, rate of..... 2909
—, manufacture 2908
Butyric ether, *see* Ethyl butyrate.
Butyrylamylaniline 2700
Butyrylbutylaniline 2700
Butyryl chloride.....2639, 2640
Butyrylethylaniline 2700
Butyrylhydrocellulose, *see* Hydrocellulose butyrate.
Butyryl methylaniline 2700
Butyrylpropylaniline 2700

Cable insulation, cellulose acetate for..... 2747
Cables, impregnation of, cellulose acetate for..... 2855
—, insulating, cellulose acetate for..... 2770
—, manufacture of, cellulose acetate for..... 2853
Cade oil 2704, 2893
Cajeputol, *see* Cineol.
Calcium acetate 2520, 2674
—, manufacture of 2614
—, manufacture acetic acid from..... 2908

Calcium acetate, manufacture acetone from..... 2528
Calcium barium acetate..... 2675
Calcium caprylate 2888
Calcium carbonate.....2567, 2614, 2805
Calcium chloride 2597
—, decreasing inflammability celluloid by..... 2901
—, dissolving cellulose formate with..... 2632
Calcium cyanide 2518
Calcium cyamide..... 2518
Calcium linoleate 2888
Calcium oleate 2888
Calcium propionate 2674
Calcium ricinoleate 2888
Calcium sulfite 2521
Calico printing, thickeners for..... 2785
Camera, motion picture..... 2878
Camphene, hydration of..... 2707
Camphene hydrochloride 2715
Camphol, *see* Borneol.
Camphor 2524, 2686, 2816, 2853
—, analysis of, in plastics..... 2923
—, artificial 2707
—, cellulose acetate plastic containing.....2765, 2785
—, cellulose acetate, plastic of 2721, 2760, 2768, 2770, 2777, 2783, 2784
—, combining cellulose acetate and cellulose nitrate with.... 2761
—, dissolving cellulose acetate with..... 2767
—, dissolving ethyl cellulose by..... 2506
—, haloids, plastic of cellulose acetate and..... 2765
—, plastic of phenylphosphate cellulose acetate and..... 2684
—, plastic properties of..... 2705
—, plastics with cellulose formate..... 2632
—, substitutes 2616, 2771
—, —, analysis of..... 2923
—, —, classification 2767, 2768
—, substitutes for 2689, 2760, 2958
—, —, glyceryl benzoates as..... 2899
—, —, glyceryl naphthoates as..... 2899
—, toughening, incandescent mantle with cellulose acetate and 2761
Camphor-methylacetanilid 2709
Camphoroids 2704
Camphor oil, *see* Oil of Camphor.
Canada balsam.....2633, 2848, 2852, 2888, 2889
Cane sugar, acetylation of..... 2644
Cannabis Indica..... 2889
Cantharis 2889
Canvas, acetating..... 2900
—, formylating 2900
—, rot-proofing, cellulose acetate for..... 2900
—, waterproofing, cellulose acetate for..... 2882
Canvas wrappers, waterproofing, cellulose acetate for..... 2806
Caoutchouc, artificial leather of cellulose acetate and..... 2809
—, combining cellulose acetate with..... 2882
—, dissolving with dichlorethylene..... 2728
—, extraction, tetrachlorethane for 2750
Capping bottles, *see* Bottles, capping.

Capsules, cellulose acetate, hydrated, manufacture..... 2881
Caraway oil, *see* Oil of caraway.
Carbanilid, *see* Diphenylurea.
Carbohydrate acetates..... 2614
Carbohydrates..... 2713
—, acetates of..... 2614
—, acetation of, zinc chloride for..... 2598
Carbolic acid, *see* Phenol.
Carbona..... 2721
Carbon bisulfide..... 2750
Carbon chlorides, purification wood cellulose with..... 2504
Carbon disulfide, *see* Carbon bisulfide.
Carbon filaments, cellulose acetate for..... 2845
Carbon paper, manufacture, cellulose acetate for..... 2817
Carbon tetrachloride..... 2566
—, acetation in presence of.....2559, 2796
—, degreasing cotton with..... 2503
—, dissolving ethyl cellulose by..... 2506
—, inhibiting acetation with..... 2606
—, insolubility hydrated cellulose acetate in..... 2575
—, manufacture of.....2721, 2722, 2723
—, —, Acker process..... 2723
—, —, Combes process.....2722, 2723
—, —, Cote process..... 2723
—, —, Danziger process..... 2723
—, —, Doerflinger process..... 2722
—, —, Dreyfus process..... 2723
—, —, Febre process..... 2723
—, —, Haworth process..... 2723
—, —, Henning process..... 2722
—, —, Machalske process..... 2723
—, —, Matthews process..... 2723
—, —, Urbain process..... 2723
—, precipitating cellulose acetate by..... 2764
—, properties..... 2722
—, purification..... 2723
—, recovery of acetic anhydride by..... 2613
—, solubility..... 2722
—, uses.....2723, 2724
Carbon trichloride, *see* Hexachlorethane.
Carbonyl chloride, manufacture of..... 2588
Cardboard, waterproofing, cellulose acetate for.....2805, 2806
Card decoration, cellulose acetate for..... 2829
Carpets, waterproofing, cellulose acetate for..... 2902
Carriage window, cellulose acetate sheet for..... 2879
Carvacrol..... 2668
Carvone.....2679, 2760, 2853
Casein..... 2860
—, cellulose acetate and..... 2861
—, cellulose acetate plastic with..... 2772
—, hardening.....2773, 2774
—, indurating.....2772, 2773
—, insulating wire with..... 2849
—, plastic, Leeman process..... 2766
—, plastic of cellulose acetate and..2667, 2668, 2669, 2772, 2774
—, plastic of cellulose acetate, borneol and..... 2776

Casein, plastic of chloral and..... 2766
—, plastic of cellulose nitrate and..... 2705
—, plastics 2771, 2772
—, —, manufacture with cellulose acetate..... 2765
—, solvent of cellulose acetate and..... 2766
—, solvents of..... 2773
Caseinates, *see also* Casein.
Casket trimmings, coating with cellulose acetate..... 2709
Castor oil, acetated.....2697, 2711
—, cellulose acetate plastic containing..... 2772
Castor oil, chloral and..... 2673
—, as plastic 2633
—, combining cellulose acetate with..... 2771
—, dissolving ethyl cellulose by..... 2506
—, miscibility of cellulose esters with..... 2574
—, nitrated 2711
—, plastic of resin, cellulose acetate and..... 2710
—, solubility of 2574
Catalyst, manufacture cellulose acetate in presence of..... 2955
—, sulfuric acid 2955
Catalysts, *see* individual chemicals.
—, ... 2538
—, neutralizing 2579
—, vanadium pentoxide 2521
Catalytic agents, *see* Catalysts.
Catalyzers 2932, 2933
Catechol, *see* Pyrocatechin.
Catechol dimethyl ether, *see* Pyrocatchin dimethyl ether.
Catechol monomethyl ether, *see* Guaiacol.
Caterpillars, formic acid in..... 2516
Caustic potash, *see* Potasium hydroxide.
Caustic soda, *see* Sodium hydroxide.
Cedar oil, *see* Oil of cedar.
Celery oil, *see* Oil of celery.
Celestron 2847
Cellit 2600, 2774, 2784, 2816
—, applications 2774, 2778, 2779
—, films of, manufacture..... 2782
—, inflammability of 2279
—, lacquers of 2782
—, manufacture of 2774, 2775, 2776
—, properties 2776, 2778
—, solubility 2776, 2782
Cellite 2774
Cellit L., *see* Cellit.
Cellobiose 2509, 2513
Cellobiose acetates 2511, 2515
Cellobiose acetosulfates 2511
Cellobiose heptacetate 2509
Cellobiose hexacetate 2509
Cellobiose octacetate
2509, 2512, 2513, 2514, 2515, 2537, 2929, 2955
—, preparation of 2510
Cellobiose octoformate 2617
Cellolite 2789
Cellon 2783, 2784, 2883, 2886

Cellon, applications 2784
—, films, efficiency of..... 2957
—, manufacture of 2783
—, treating fabrics with..... 2886
Cellon-Emaillit 2886
Cellon lacquer 2887
Cellone 2789
Cellonit 2789
Celluloid 2505
—, automobile shields of..... 2871
—, benzyldihydrocarvone and 2760
—, cleansing, Pueschel process..... 2771
—, collars, inflammability, decreasing with cellulose acetate.. 2900
—, collars of 2900
—, cuffs of 2900
—, decreasing inflammability of, by calcium chloride..... 2901
—, —, by cellulose acetate 2901
—, film cement of..... 2956
—, impregnating textiles with..... 2813
—, incombustible, *see also* Celludoid, uninflammable.
—, —, ... 2761
—, —, Schmerber and Morane process..... 2650
—, inflammability, decreasing by ammonium chloride..... 2901
—, —, decreasing with cellulose acetate..... 2900
—, —, reducing 2761
—, —, —, Nishida process 2653
—, manufacture artificial leather of..... 2809
—, medical jackets of..... 2890
—, non-inflammable 2760, 2786
—, —, recipes for 2760
—, plastic of *o*-tricresyl phosphate and..... 2810
—, solvent of 2727
—, splints of 2890
—, substitute, Apyroid 2789
—, —, Argonite 2789
—, —, Boroid 2789
—, —, casein and cellulose acetate..... 2773
—, —, Cellit 2775, 2777, 2778, 2779
—, —, Cellolite 2789
—, —, Cellone 2789
—, —, Cellonit 2789
—, —, cellulose acetate and casein..... 2773
—, —, cellulose acetate as.....2748, 2784
—, —, Manissadjian 2762
—, substitute for 2759
—, surgical jackets of..... 2890
—, uniflammable, *see also* Celluloid incombustible.
—, —, Reeser process 2765
—, —, Schmerber process 2761
—, waterproofing with 2806
—, wind shields of..... 2871
Celluloid substitute 2581
—, cellulose acetate and trichlorethylene..... 2732
—, Dreyfus' 2732
—, Koller's 2732
—, uninflammable 2581

Cellulose, *see also* Cotton, Paper, Wood.
—, ... 2501
—, acetated, see Cellulose acetate.
—, acetation
2512, 2526, 2532, 2560, 2562, 2564, 2566, 2796, 2897, 2900
—, —, Althausse process 2558
—, —, anhydrochlorides for 2602
—, —, ant-acids in 2823
—, —, apparatus for 2608
—, —, continuous 2769
—, —, Badische process 2563, 2929
—, —, Bayer process 2560, 2576
—, —, Boesch process 2562
—, —, catalyzers for 2930, 2932
—, —, Chemische Fabrik von Heyden process 2577
—, —, chloracetic acids for 2600, 2601
—, —, chlorides for 2601
—, —, commercial methods of 2567, 2568, 2569
—, —, Corti process 2593
—, —, Cross and Bevan method 2556
—, —, Danzer process 2576
—, —, details of 2567, 2568, 2569, 2570, 2571
—, —, dimethyl sulfate for 2930
—, —, Dreyfus process 2586
—, —, Eichengruen and Becker process 2560
—, —, Franchimont method 2929
—, —, Grote process 2566, 2770
—, —, Henckel-Donnersmarck process 2558
—, —, hydration after 2553
—, —, hydrochloric acid for 2603
—, —, incomplete 2555
—, —, inhibiting 2556, 2557
—, —, Knoll process 2577
—, —, Landsberg process 2566
—, —, Lederer process 2558, 2605, 2929
—, —, maximum 2939
—, —, Miles process 2567, 2575, 2929
—, —, Mork process 2605
—, —, nitric acid for 2603
—, —, partial 2843, 2844
—, —, Paschke process 2596
—, —, Peters and Cullum process 2565
—, —, process for 2928, 2930
—, —, recovery acetic acid 2612
—, —, recovery acetic anhydride 2613
—, —, Skraup and Koenig method 2929
—, —, Societe Chimique des Usine du Rhone process 2606
—, —, Societe Debauge process 2605
—, —, Sthamer process 2559
—, —, sulfacetic acid for 2601
—, —, sulfinic acids for 2821, 2930
—, —, sulfonic acids for 2930
—, —, sulfur chlorides for 2603
—, —, sulfuric acid in 2928, 2929
—, —, sulfuryl chloride for 2602
—, —, superficial 2555, 2843, 2844, 2845, 2863, 2867

Cellulose, acetation, Weber and Cross method..... 2557
—, —, without change in form.....2559, 2769
—, —, Wohl process 2575
—, —, yield 2575, 2819
—, —, zinc chloride in.....2575, 2599, 2930
Cellulose, acetolysis of 2513
—, acetophosphates 2822
—, acetosulfates 2930
—, acetylated, *see* Cellulose, acetation.
—, acetylation, *see* Cellulose, acetation.
—, acetylized, *see* Cellulose acetate.
—, acylation, *see* Cellulose nitration and acetation.
—, action of acetic acid on..... 2568
—, alkylation, *see also* Cellulose ethylation and methylation.
—, alkylation of 2505, 2897
—, anhydrous, preparing 2513
—, ash in, determination of..... 2502
—, benzoylation of 2565, 2897
—, bleaching 2611
—, chlorides of 2508
—, conversion to dextrose pentacetate..... 2515
—, cuproammonium, acetylation of..... 2555
—, decomposition of, indications..... 2941
—, —, by contact substances..... 2513
—, determination water in..... 2502
—, dyeing before acetation..... 2841
—, dyeing before acidylation..... 2628
—, esterification, *see* Cellulose, acetation or nitration.
—, esterification of 2526
—, etherification of 2505
—, ethers of, *see* Methyl, etc., cellulose.
—, —, ... 2505
—, ethyl, solvents of 2506
—, ethylation, *see also* Cellulose, alkylation.
—, ethylation of 2505
—, fat in, determination of..... 2502
—, formation of, from viscose..... 2628
—, formula of 2931
—, formylation, see also Cellulose formate.
—, —, ...2520, 2617, 2618, 2619, 2620, 2900
—, —, chlorosulfonic acids for..... 2621
—, —, ethyl-sulfuric acid for..... 2621
—, —, halogens for 2621
—, —, hydrochloric acid for..... 2621
—, —, phenolsulfonic acids for..... 2621
—, —, pyrosulfuryl chloride for..... 2621
—, —, sulfonates for..... 2621
—, —, sulfuric acid for..... 2620
—, —, sulfuryl chloride for..... 2621
—, —, zinc chloride for..... 2621
—, formylized, *see also* Cellulose formate.
—, hemicellulose in, determination of..... 2502
—, hydrate of, acetation.....2555, 2556
—, hydrated, acetation of.....2555, 2556
—, —, capping bottles with..... 2881
—, hydrolysis of.....2513, 2514, 2536, 2537, 2563, 2605

Cellulose, hydrolysis to dextrose 2515
—, hydrolyzed, acetylation of 2605
—, hydrolyzing with glycerol 2565
—, hygroscopicity of 2514
—, maize stem 2504
—, manufacture mixed esters of 2537
—, mercerized, acetylation of 2928, 2964
—, methylated, acetation of 2508
—, —, hydrolysis of 2897
—, —, methoxyl groups in 2897
—, —, properties of 2508
—, methylation of 2505, 2897, 2898
—, —, process for 2508
—, methylation, *see also* Cellulose alkylation.
—, modified, *see* Hydrocellulose, Oxycellulose.
—, —, acetylation of 2555
—, moisture in 2567
—, nitration 2930, 2942
—, —, apparatus for 2608
—, —, maximum 2945
—, obtaining from cotton seed hulls 2502
—, origin of 2502
—, oxycellulose in, determination of 2502
—, phenyl 2657
—, preparation for acetation 2554
—, preparation for esterification 2504
—, scouring 2567, 2568
—, soluble 2888
—, solvent for 2625
—, solvent, hydrochloric acid as 2614
—, structure of 2759
—, sulfite, esterification of 2504
—, sulfonation of 2654
—, sulpholysis of 2514
—, tetraphenyl 2657
—, water in, determination of 2502
—, wood, acetated, hydration of 2505
—, —, acetates of 2504
—, —, esterification of 2504
—, —, purification, solvents for 2504
—, xanthates of, *see* Viscose.
—, zinc chloride solvent of 2533
Cellulose acetate, *see also* Cellulose mono-, di-, tri-acetate.
—, acetic acid in, determining 2921, 2922, 2923
—, —, —, Green and Perkin method 2923
—, —, —, Ost method 2922
—, acetic acid insoluble 2607
—, acetic acid solutions of 2525
—, acetone-insoluble 2955
—, acetone-soluble, manufacture of 2567, 2581, 2776
—, acid in, pyridine for neutralizing 2853
—, action alcohol and benzene on 2758
—, action ultra violet rays upon 2863
—, alcohol-insoluble 2598
—, alcohol (70%) soluble 2561
—, alcohol soluble 2663

Cellulose acetate, alcohol soluble, manufacture of, 2560, 2562, 2777, 2930
—, —, uses of ... 2892
—, analysis ... 2637
—, —, ash in ... 2917
—, —, Barthelemy method ... 2924
—, —, Cross and Bevan method ... 2923
—, —, determining sulfuric acid in ... 2926
—, —, Eberstadt method ... 2925
—, —, moisture in ... 2917
—, —, Schwalbe method ... 2924
—, —, solubility ... 2917, 2918
—, anhydrous ... 2581
—, —, lacquers containing ... 2749
—, anti-fouling paint of ... 2772
—, artificial filaments of ... 2817
—, artificial leather of ... 2885
—, artificial sponge of ... 2956
—, ash in, determining ... 2917
—, automobile shields of ... 2871
—, bands, hydrating ... 2578
—, benzene-insoluble ... 2598
—, bleaching ... 2572, 2600, 2611, 2793
—, —, electrolytically ... 2612
—, —, potassium permanganate for ... 2612
—, —, sodium peroxide for ... 2612
—, bleaching and hydrating ... 2612
—, capping bottles with ... 2881
—, casein and ... 2861
—, casein plastics containing ... 2771, 2772
—, cellulose nitrate and ... 2651
—, cement of ... 2901
—, cementing leather with ... 2901
—, chemistry of ... 2544
—, chloroform insoluble ... 2607
—, chloroform-soluble, manufacture of ... 2553, 2776
—, clarification ... 2875
—, cleansing, Pueschel process ... 2771
—, coating cigar tips with ... 2887
—, coating cloth with ... 2811
—, coating fabrics with wood meal and ... 2900
—, coating furs with ... 2815
—, coating gelatin with ... 2813
—, coating hides with ... 2814
—, coating leather with ... 2814
—, coating patent leather with ... 2814
—, coating shellac with ... 2902
—, coating viscose with ... 2813
—, colloidal nature of ... 2538
—, combining, boric acid with ... 2902
—, —, cellulose nitrate with ... 2676, 2747, 2761, 2902
—, —, caoutchouc with ... 2882
—, —, casein with ... 2773
—, —, dihydroxydiphenyldimethylmethane with ... 2904
—, —, jelutong resin with ... 2772
—, —, mercaptals with ... 2902
—, —, mercaptans with ... 2902

Cellulose acetate, combining, nitrotoluols with..... 2902
—, —, polysulfides with 2902
—, —, rubber with 2887
—, —, rubber resin with..... 2772
—, —, sulfides with 2902
—, —, sulfinic acid with..... 2902
—, —, sulfones with 2902
—, —, sulfonic acid with..... 2902
—, —, sulfoxides with 2902
—, —, sulfur with 2901
—, comparison with nitrocellulose..... 2759
—, condensation products and..... 2772
—, conductive capacity 2760
—, copper number of, determining..... 2920
—, cosmetics of 2889
—, cost of production 2760
—, covering spinning rollers with..... 2903
—, cresol, casein and 2861
—, decomposition of.....2550, 2561, 2932
—, —, indications 2941
—, decreasing inflammability of celluloid by..... 2901
—, diacetyltartrate as solvents for..... 2608
—, differential mercerization by..... 2845
—, dissolving 2823
—, dissolving in acetic acid..... 2892
—, dyeing.....2612, 2759, 2786, 2835, 2837, 2838, 2839, 2843
—, —, algol colors for..... 2851
—, —, aniline black for..... 2839
—, —, aniline yellow for..... 2839
—, —, azo, Turkey red for..... 2839
—, —, azochromin for 2839
—, —, bismark brown for..... 2839
—, —, Borzykowski process 2842
—, —, cibal colors for..... 2841
—, —, helindon colors 2841
—, —, immedial colors for..... 2841
—, —, indanthrene colors for..... 2841
—, —, katigen colors for..... 2841
—, —, α-naphthylamine bordeaux for..... 2839
—, —, nitranilin red for..... 2839
—, —, penetrating dyestuffs in..... 2836
—, —, real red E for..... 2840
—, —, rosanthrene colors for..... 2841
—, —, soudan I for 2839
—, —, soudan III for..... 2839
—, edible preparations of..... 2889
—, emulsions of 2857
—, enameling leather with..... 2814
—, epichlorhydrin-soluble, manufacture..... 2776
—, ether-insoluble 2598
—, ethyl phthalate and 2695
—, explosives containing..... 2902
—, explosives of 2846
—, fibrous 2547
—, —, hydrating 2583
—, —, manufacture of 2564, 2604

Cellulose acetate, filaments, carbon..... 2845
—, filling thread with..... 2823
—, film, continuous, manufacture, Bonwitt process..... 2869
—, —, manufacture 2899, 2902
—, —, recovery of constituents from..... 2807
—, —, waste, utilizing 2792, 2874
—, —, cement of 2956
—, films, brittleness in, overcoming..... 2769
—, —, hydrating 2578
—, —, manufacture 2781
—, —, photographic 2898
—, —, testing 2871
—, filtration 2875
—, fixation on textiles..... 2787
—, flexibility of, sulforicinoleic acid for..... 2587
—, formic acid soluble..... 2607
—, gelatinizing 2765, 2781
—, gilding lace with..... 2804
—, glass substitute 2879
—, glazing linen with..... 2804
—, glycerol-soluble 2598, 2666
—, guaiacol, casein and..... 2861
—, historical 2530
—, hydrated, capping bottles with..... 2881
—, —, discovery of 2553, 2554
—, —, properties of 2575
—, —, testing 2573
—, hydrating, fibrous 2583
—, —, Mork process 2584
—, hydration of 2553, 2571, 2599, 2661
—, —, Bayer process 2576
—, —, catalyzers for 2577
—, —, chlorides for 2577
—, —, Danzer process 2576
—, —, Dreyfus process 2583
—, —, von Heyden process..... 2577
—, —, Knoll process 2577
—, —, Miles process 2574, 2575
—, —, Mork process 2840, 2861, 2862
—, —, nitrates for 2577
—, —, Panthonier process 2582
—, —, sulfates for 2577
—, —, sulfuric acid for..... 2577
—, hydrolysis of 2955
—, —, aniline for 2578
—, —, Chem. Fabr. auf. Actien process..... 2579
—, —, Lederer process 2578
—, —, sulfacetic acid for..... 2578
—, —, toluidine for 2578
—, —, Verein f. Chem. Ind. Mainz process..... 2579
—, —, xylidine for 2578
—, imitation glass of..... 2899
—, imitation leather of..... 2885
—, impregnating asbestos with..... 2813
—, impregnating cables with..... 2855
—, impregnating incandescent mantles with..... 2855

Cellulose acetate, impregnating paper with..... 2816
—, impregnating wings with..... 2885
—, incorporating coumarone with..... 2904
—, incorporating indene with..... 2904
—, increasing stability of explosives by..... 2846
—, indicating decomposition in smokeless powder by..... 2846
—, inflammability, decreasing 2608
—, —, decreasing with borax..... 2608
—, —, increasing by cellulose nitrate..... 2856
—, infusible, manufacture 2957
—, insoluble, converting 2958
—, insulating properties of.....2851, 2852
—, insulating with 2847
—, insulating wire with..... 2847
—, lacquer.....2747, 2748, 2789, 2882, 2883
—, —, camphor substitutes for..... 2795
—, —, coloring leather with..... 2932
—, —, diacetone alcohol for..... 2718
—, —, formulae 2782
—, —, inflammability, reducing 2793
—, —, Leduc Heitz formula..... 2806
—, —, manufacture 2903, 2904
—, —, preserving documents with..... 2816
—, —, properties 2789
—, —, protecting legal papers with..... 2817
—, —, tipping stays with..... 2798
—, lakes containing 2560
—, leather, artificial 2811
—, mantles, incandescent, toughening with..... 2664
—, manufacture 2777, 2835, 2903, 2955
—, —, acetic anhydride vapours for..... 2903
—, —, Badische process 2904
—, —, Corti process 2593
—, —, Dreyfus process 2586
—, —, Eichengrun process 2774
—, —, Fabr. Chem. Produkten process..... 2957
—, —, Fabr. de Produits Chimique Flora process..... 2593
—, —, Knoll & Co. process.....2581, 2957
—, —, Lederer process 2774, 2958
—, —, methods for 2552
—, —, Miles process 2574, 2575
—, —, Parkin and Williams process..... 2581
—, —, Paschke process 2596
—, —, Plinatus process 2578
—, —, Ramsey method 2903
—, —, Safety Celluloid Co. process..... 2596
—, —, Soc. Chem. Industry process.....2762
—, —, Societe L'Oyonnithe process..... 2587
—, —, soluble in ethyl acetate..... 2903
—, —, Verein Chem. Ind. process..... 2957
—, —, Wohl process 2587
—, —, zinc chloride for..... 2598
—, manufacture acetone soluble..... 2775
—, manufacture artificial pearls by..... 2903
—, manufacture artificial rubber with..... 2884
—, manufacture artificial sponge from..... 2835

Cellulose acetate, manufacture artificial wood with..... 2855
—, manufacture bushings from..... 2851
—, manufacture capsules of hydrated..... 2881
—, manufacture carbon papers with..... 2817
—, manufacture carpets with..... 2902
—, manufacture lincrusta with..... 2902
—, manufacture metallized fabrics with.....2812, 2813
—, manufacture orthopedic appliances of..... 2900
—, manufacture plastics of casein and..... 2765
—, manufacture rubber foam with..... 2886
—, manufacture surgical splints with..... 2900
—, manufacture stereotype paper with..... 2817
—, manufacture stereotypes with..... 2855
—, manufacture veilings with..... 2827
—, medical jackets of..... 2890
—, mercerization 2759
—, metallizing lace with..... 2804
—, methods of manufacture..... 2552
—, moisture, determining 2917
—, molecular weight of, determining..... 2921
—, nitrated, solvents 2745
—, nitrating.....2537, 2597, 2650, 2651, 2652
—, nitrobenzene-soluble, manufacture 2776
—, nitromethane as solvent for.....2608, 2703
—, nonsolvents of 2604
—, optical behavior of..... 2828
—, pharmaceutical uses of.....2888, 2889
—, phenol, casein and..... 2861
—, phonograph composition containing.....2879, 2880
—, phonograph records of..... 2879
—, photographic emulsion of..... 2857
—, plastic 2575, 2664, 2760, 2768
—, plastic, acetin for.....2762, 2771
—, —, asbestos with 2768
—, —, Beatty process 2767
—, —, Bume process 2761
—, —, camphor 2761, 2770, 2783, 2784
—, —, carvone for 2760
—, —, casein and 2668, 2774
—, —, casein containing 2772
—, —, castor oil in..... 2762
—, —, cellulose nitrate containing..... 2762
—, —, Charuel process 2770
—, —, classification 2767
—, —, Convert process 2749, 2750
—, —, dichlorethylene in 2728
—, —, dihydroxydiphenyldimethylmethane containing 2767
—, —, Dreyfus process.....2753, 2768
—, —, earth-nut cake containing..... 2774
—, —, Eichengrun process 2768
—, —, epichlorhydrin for..... 2738
—, —, gelatin for..... 2761
—, —, glycose containing 2774
—, —, graphite with..... 2768
—, —, hexachlorethane 2755
—, —, hydroaromatic ketones containing..... 2760

Cellulose acetate, plastic, Ichenhauser process..... 2769
—, —, Knoll & Co. process.....2769, 2771
—, —, Lederer process 2763
—, —, Lindsay process.....2761, 2767, 2770
—, —, manol 2771
—, —, manufacture 2764, 2783
—, —, —, Eichengrun process 2783, 2784
—, —, —, Lehmann process 2903
—, —, —, Reeser process 2765, 2784
—, —, —, Richter process 2765
—, —, manufacture with casein..... 2765
—, —, manufacture with creosote..... 2784
—, —, manufacture with phenol..... 2765
—, —, Meyer process 2771
—, —, mica with 2768
—, —, Mijnessen process 2761
—, —, phenol-aldehyde 2766
—, —, pulegone for..... 2760
—, —, pyrocatechin 2766
—, —, pyrocatechin diethyl ether..... 2766
—, —, Reeser process 2765
—, —, resins for 2764
—, —, shellac and 2766
—, —, tetrachlorethane 2762, 2763
—, —, turpentine 2766
—, —, vaseline 2766
—, —, viscose and 2774
—, —, Walker process 2761
—, —, wax 2766
—, plasticity of 2575
—, polarization of 2547
—, porosity of, increasing.....2837, 2838
—, precipitating 2815
—, alcohol for 2557
—, preserving aroma of tobacco by..... 2887
—, preserving wood with..... 2854
—, printing bronze and..... 2829
—, printing composition of..... 2667
—, printing, mica and..... 2829
—, printing on, ink for..... 2806
—, printing on textiles with..... 2806
—, printing on textiles with condensation products and..... 2787
—, printing plates of..... 2899
—, printing with 2903
—, properties of 2550, 2759
—, protecting drying cylinders from erosion by..... 2540
—, protecting legal papers with..... 2817
—, protecting phonograph records with..... 2902
—, purifying 2562
—, pyridine-soluble, manufacture..... 2776
—, recovering 2793
—, removing warts with..... 2889
—, recovery of (from film)..... 2875
—, refraction of 2547
—, reinforcing celluloid collrs with..... 2900
—, resistivity 2854

Cellulose acetate, rotation of..... 2547
—, rot-proofing canvas with..... 2900
—, salves of 2889
—, saponification, *see also* Cellulose acetate, hydration.
—, —, ...2585, 2947, 2949, 2950
—, —, Mork process 2840
—, soluble, increasing.....2957, 2958
—, solvents for 2932
—, stabilizing 2930
—, sulfonic acid 2654
—, sulfuric acid 2654
—, sulfuric acid esters..... 2944
—, tartrates as solvent for..... 2608
—, tensile strength of, determining..... 2919
—, thermoplastic 2760
—, tetrachlorethane solvent of.....2744, 2745
—, threads, hydrating 2578
—, sheets of 2860
—, sheets, brittleness in, overcoming..... 2769
—, —, Cathelineau process 2861
—, —, cleansing 2771
—, —, hydrating 2584
—, —, manufacture of..... 2771
—, —, —, with pentachlorethane 2752
—, —, —, Mork porcess 2861
—, —, renovating 2771
—, shields, wind 2871
—, silvering lace with..... 2804
—, softeners for 2826
—, softening 2823
—, solidifying alcohol with..... 2890
—, solubility 2579, 2661
—, determinations of.....2660, 2917, 2918
—, —, increasing 2955
—, —, modifying..2576, 2577, 2578, 2579, 2582, 2583, 2903, 2904
—, solutions of, neutral..... 2585
—, —, viscosity, increasing 2853
—, —, preserving 2821
—, solvent, amyl acetate..... 2665
—, —, amyl alcohol 2665
—, —, anethol 2666
—, —, antimony trichloride for..... 2665
—, —, apiol 2666
—, —, benzyl alcohol 2665
—, —, butylene glycol 2666
—, —, casein and 2766
—, —, dichlorethylene and alcohol 2664
—, —, ethyl-*b*-naphthol 2666
—, —, glycerol 2666
—, —, glyceryl acetate 2666
—, —, glycol 2666
—, —, guaiacol 2666
—, —, isoeugenol 2666
—, —, isosafrol 2666
—, —, methyl alcohol 2665
—, —, methyl-*a*-naphthol 2666

Cellulose acetate, solvent, naphthol..... 2666
—, —, pentachlorethane and alcohol..... 2664
—, —, pyrogalol 2666
—, —, resorcinol 2666
—, —, resorcinol dimethyl ether..... 2666
—, —, resorcinol monomethyl ether..... 2666
—, —, safrol 2666
—, —, tin chloride 2665
—, —, toluene and alcohol..... 2664
—, —, trichlorphenol 2666
—, —, veratrol 2666
—, solvents 2661, 2761, 2762, 2783, 2800
—, —, alcohols 2662
—, —, classification 2662, 2768
—, —, ethyl alcohol 2662
—, —, formic acid 2821
—, —, glycerol benzoates as..... 2899
—, —, glyceryl naphthoates as..... 2899
—, —, Lindsay's classification..... 2703
—, —, mixed 2753
—, —, pentachlorethane 2752
—, —, recovery of 2718
—, specific conductive capacity..... 2760
—, specific inductive capacity..... 2854
—, splints of 2890
—, stability 2610
—, —, determining 2919, 2920
—, stiffening felt with..... 2815
—, stiffening hats with..... 2815
—, supple, *see* Cellulose acetate, plastic.
—, surgical jackets of..... 2890
—, swelling 2823
—, —, increasing absorptive power of dyestuffs by..... 2837
—, synthetic India rubber of..... 2901
—, uninflammable, Manissadjian process..... 2762
.., use of, for sofetening corns..... 2889
—, —, in air-craft manufacture..... 2882
—, —, in cable manufacture..... 2853
—, —, in cuts 2889
—, —, in medicine 2889
—, —, in wounds 2889
—, varnishes of 2903
—, —, phenol-aldehyde and 2772
—, —, viscosity, determining 2918
—, —, Cochius method 2918
—, —, Henry method 2918
—, viscosity of solutions of..... 2547
—, —, viscous, manufacture 2957
—, waterproof cement of..... 2901
—, waterproofing 2869, 2899
—, —, aeroplane canvas with..... 2882
—, —, balloon fabric with..... 2813
—, —, collars with 2900
—, —, fabrics with 2900
—, —, textiles with 2806
—, —, viscose with 2855

Cellulose acetate, water-soluble 2598
—, wind shields of..... 2871
—, window panes of..... 2879
Cellulose acetate sulfonic acid..... 2654
Cellulose acetate sulfuric acid..... 2654
Cellulose acetates, classification..... 2925
Cellulose acetobenzoate 2656
—, combining casein with..... 2773
Cellulose acetobutyrate 2640, 2653
Cellulose acetonitrate 2548, 2597, 2648, 2746
—, denitration 2649
—, manufacture of 2835
—, —, Akt. Ges. f. Anilin Fabr. process..... 2652
—, —, Berl and Smith process..... 2650
—, —, Nishida process 2652
—, —, Florentin process 2652
Cellulose acetopalmitate 2774
Cellulose acetophenylate, *see* Cellulose phenylacetate.
Cellulose acetophosphat 2822
Cellulose acetopropionate.....2604, 2636, 2653
Cellulose acetosulfate.....2510, 2653, 2948, 2949
—, analysis of 2923
—, saponification of..... 2923
Cellulose alkyl esters, *see also* Cellulose esters.
—, manufacture 2903
Cellulose angelate 2640
Cellulose benzoacetate 2640
Cellulose benzoate 2544, 2641, 2654, 2658
—, analysis 2923
—, increasing stability of explosives by..... 2846
—, manufacture of 2641
—, —, Akt. Ges. f. Anil. Fabr. method..... 2658
—, manufacture stereotypes with..... 2855
—, manufacture, Wohl process..... 2656
—, plastics 2658
—, properties 2657
—, solubility 2657
—, saponification of 2923
Cellulose benzoylnitrate 2656
Cellulose butyrate.....2548, 2637, 2639, 2731, 2736, 2738, 2804
—, applications 2639
—, combining casein with..... 2773
—, condensation products and..... 2772
—, manufacture, Lederer process..... 2640
—, —, Weber and Cross process..... 2639
—, uses of 2639
Cellulose butyroacetate, *see* Cellulose acetobutyrate.
Cellulose caprate 2640
Cellulose caproate 2640
Cellulose chloracetate 2604
Cellulose chlorbenzoate 2544
Cellulose chloride 2614
Cellulose dextrins, acetylated 2510
—, acid esters of..... 2514
Cellulose diacetate.....2537, 2545, 2925
—, formula of 2544

Cellulose diacetate, manufacture of 2545
—, manufacture from cellulose triacetate 2840
—, properties of 2545, 2932
—, solubility 2680
Cellulose diacetylmonoformate 2622
Cellulose dibenzoate 2655, 2656, 2657
—, properties 2657
—, solubility 2657
Cellulose dinitrate-dinitrobenzoate 2657
Cellulose dodecanitrate 2618
Cellulose enanthate, *see* Cellulose oenanthate.
Cellulose esters, analysis of 2905, 2922
—, dyeing 2835
—, hydrolysis of 2579
—, inflammability, reducing 2610
—, manufacture mixed 2537
—, materials entering into 2501
—, miscibility with castor oil 2574
—, mixed 2649
—, partial saponification of 2585
—, separating, ethyl alcohol for 2663
—, uninflammable, analysis of 2905
—, —, properties of 2759
—, —, uses of 2759
Cellulose formate, *see also* Cellulose formylation.
—, ... 2544, 2616, 2731, 2749, 2809
—, amyl lactate and 2633
—, artificial filaments of 2824
—, chlorosulfonic acid for manufacture of 2626
—, condensation products and 2772
—, dissolving 2632, 2680
—, dyeing 2839, 2840, 2841, 2842
—, fibrous 2619
—, films from 2629
—, formic acid solvent for 2520
—, hydration of 2627, 2634
—, impregnating aeroplane wings with 2885
—, manufacture of 2620
—, —, Act. Ges. f. Anilin Fabr. process 2625
—, —, Bemberg process 2634
—, —, Deming process 2625
—, —, Dreyfus process 2626
—, —, Nitritfabrik process 2624
—, —, Vereingte Glanstoff process 2627
—, manufacture stereotypes with 2855
—, methyl acetone and 2633
—, nonsolvents of 2623
—, plastic 2631, 2633, 2762
—, —, amyl lactate and 2633
—, —, artificial silk of 2633
—, —, castor oil and 2633
—, —, methyl acetone and 2633
—, —, methyl ethyl ketone and 2633
—, plastics with camphor 2632
—, pyridine-soluble 2626
—, solvents of 2623, 2632, 2800

Cellulose formate, sulfuryl chloride for manufacture..... 2626
—, uses 2629
Cellulose heptaacetate 2925
Cellulose heptylate 2640
Cellulose hexacetate 2925
—, properties 2932
Cellulose hexanitrate 2945
Cellulose hexanoate 2640
Cellulose hybogeate 2640
Cellulose hydrate, acetation of..... 2556
—, benzoylation 2655
—, capping bottles with..... 2881
—, formation of, from viscose..... 2628
—, formylation of 2627
—, manufacture of cellulose formate from..... 2620
—, preparation of 2534
Cellulose monoacetate 2545, 2925
—, formula for 2544
—, manufacture of 2545
—, properties of 2545, 2932
—, solubility of 2545, 2680
Cellulose monobenzoate.....2654, 2655, 2657
Cellulose mono-*p*-chlorbenzoate 2657
Cellulose monoformate, *see also* Cellulose formate.
—, ... 2623
—, manufacture of.....2623, 2624
Cellulose nitracetate 2597
Cellulose nitrate, acetated, solvents..... 2745
—, acetation of.....2537, 2597, 2648, 2650, 2652
—, artificial filaments of..... 2957
—, artificial sponge for..... 2956
—, brisance of, modifying by cellulose acetate..... 2846
—, cellulose acetate and..... 2651
—, cellulose benzoate and..... 2658
—, cleansing, Pueschel process..... 2771
—, combining cellulose acetate with.2676, 2747, 2761, 2769, 2902
—, combining nitrotoluols with 2902
—, combining viscose with..... 2901
—, coating cigar tips with..... 2887
—, coating leather with..... 2814
—, coating yarn with.....2825, 2826
—, denitrated, testing..... 2831
—, combining dihydroxydiphenyldimethylmethane with..... 2904
—, denitrated, formylating..... 2620
—, epichlohhydrin solvent for..... 2737
—, ethyl phthalate and..... 2695
—, gilding lace with..... 2804
—, glazing linen with..... 2804
—, impregnating aeroplane wings with..... 2885
—, impregnating cigar tips with..... 2888
—, impregnating hats with..... 2815
—, inflammability, reducing..... 2649
—, insulating wire with..... 2851
—, insulating with..... 2853
—, iridescent films of..... 2824
—, lacquering documents with..... 2816

Cellulose nitrate, lacquers, coloring leather with..... 2932
—, —, covering with..... 2903
—, —, uninflammable 2720
—, mantle dip of gelatin and..... 2856
—, manufacture artificial sponge from..... 2835
—, manufacture from hydrocellulose..... 2531
—, metallising lace with..... 2804
—, nitromethane as solvent for..... 2703
—, plastic of casein and..... 2705
—, plastic of cellulose acetate and.....2651, 2762
—, plastic of coumarone and..... 2904
—, plastic, Dreyfus..... 2768
—, plastic of indene and..... 2904
—, plastic, manol and..... 2771
—, plastics containing..... 2760
—, preserving aroma of tobacco by..... 2887
—, recovery of (from film)..... 2875
—, sheets, cleansing..... 2771
—, —, renovating 2771
—, silvering lace with..... 2804
—, solidifying alcohol by..... 2891
—, solvents, classification..... 2768
—, solvents of.....2529, 2800
—, substitute for..... 2759
—, toughening incandescent mantles with..... 2856
—, viscosity of..... 2547
—, waterproofing 2806
—, waterproofing film with.....2869, 2870, 2898
—, waterproofing viscose with..... 2855
Cellulose nitrates, discovery..... 2659
Cellulose nitroacetates, *see* Cellulose acetonitrates.
Cellulose nitrobenzoate, *see* Cellulose benzonitrate.
Cellulose octacetate..... 2925
Cellulose oenanthate..... 2640
Cellulose oleate..... 2640
Cellulose palmitate.....2653, 2731, 2774
—, combining casein with..... 2773
—, condensation products and..... 2772
Cellulose pentacetate 2547, 2549, 2925
—, properties 2932
Cellulose phenylacetate.....2640, 2653
—, combining casein with..... 2773
Cellulose phenylpropionate..... 2640
Cellulose phosphoacetate..... 2640
Cellulose phosphoformates..... 2621, 2632
Cellulose propioacetate, *see* Cellulose acetopropionate.
Cellulose propionate.....2604, 2634, 2638, 2749
—, hydration of..... 2639
—, increasing stability of explosives by..... 2846
—, manufacture, Actien Ges. f. Anilin Fabr. process..... 2636
—, —, Claessen process..... 2635
—, —, Knoll & Co. process..... 2635
—, —, Lederer process..... 2636
—, —, Weber and Cross process..... 2634
—, properties 2638
—, solvents of..... 2636

Cellulose propionate, solubility 2638
Cellulose ricinoleate..... 2587
Cellulose sebacate.....2639. 2640
Cellulose stearate..... 2640
Cellulose sulfacetate, *see also* Cellulose acetosulfate.
—, manufacture stereotypes with..... 2855
Cellulose sulfate 2855
Cellulose sulfocarbonate, *see also* Cellulose xanthate.
Cellulose sulfochloride..... 2654
Cellulose sulfonate..... 2654
—, solubility 2654
Cellulose sulfuric acid..... 2943
Cellulose tetracetate.....2547, 2925, 2928
—, manufacture, Henckel-Donnersmarck process..... 2549
—, polemical on..... 2537
—, properties 2932
—, solubility of..... 2548
Cellulose tetrabenzoate..... 2656
Cellulose thiocyanate..... 2623
Cellulose toluenesulfonate..... 2654
Cellulose triacetate, *see also* Cellulose acetate.
Cellulose triacetate.....2545, 2925
—, hydrated 2570
—, manufacture of.....2566, 2567, 2568, 2569, 2570, 2571
—, properties of.....2545, 2546. 2547, 2570, 2932
—, solubility in glacial acetic acid..... 2554
—, solubility of..... 2546
—, swelling in water of..... 2546
Cellulose tribenzoate..... 2657
Cellulose trinitrate-dinitrobenzoate 2657
Cellulose tripropionate 2638
Cellulose valerate.....2637, 2638
Cellulose xanthate, *see also* Viscose.
—, ... 2888
—, plastic of cellulose acetate and..... 2774
Cellulose xanthogenate, *see* Cellulose xanthate.
Celluloses 2502
—, differentiation between..... 2502
Cements, cellulose acetate..... 2900
—, manufacture of cellulose acetate containing..... 2566
—, waterproof, cellulose acetate..... 2901
Ceresin 2711
Ceric oxide..... 2907
Cerium, manufacture acetic acid with aldehyde and compounds of 2522
Chalk, polishing linen with..... 2805
Chamber crystals, *see* Nitrosyl sulfate.
Chinese gold paint..... 2801
Chinese wood oil, *see* Tung oil.
Chloracetamide 2734
Chloracetanilid 2705
Chloracetic acid, *see also* Mono-, Di-, and Tri- chloracetic acid.
Chloracetic (mono) acid, hydrating cellulose acetate with.... 2576
Chloracetic acids.....2637, 2747, 2805
—, acetation with..... 2600
—, manufacture cellulose propionate with..... 2636

Chloracetic ester..... 2734
Chloracetic ether..... 2734
Chloracetone 2701
Chloracetyl glycogens 2616
Chloracetylene 2732
Chloral 2629, 2641, 2672, 2768, 2735, 2889
—, castor oil and..... 2673
—, cellulose acetate plastic containing..... 2760
—, manufacture pentachlorethane from..... 2751
—, plastic of cellulose acetate, casein and..... 2766
—, plastic cellulose benzoate and..... 2658
Chloral alcoholate.....2630, 2667, 2672, 2673, 2710, 2745, 2760
Chloral alkyloxide, *see* Chloral alcoholate.
Chloral hydrate.....
2630, 2633, 2667, 2672, 2673, 2686, 2730, 2745, 2747, 2773
—, camphor and..... 2710
—, hydrating cellulose esters with..... 2582
—, plastic of cellulose acetate and.....2760, 2763
—, removing corns by cellulose acetate and..... 2889
Chloramyl, *see* Amyl chloride.
Chloranisol 2630, 2728
Chlorbenzene 2711, 2885
—, dissolving cellulose acetate and casein with..... 2773
p-Chlorbenzenesulfanilid 2714
p-Chlorbenzenesulfo-*b*-napthol 2714
p-Chlorbenzoyl chloride.....2544 2657
Chlorbenzol, *see* Chlorbenzene.
Chlorbenzyl alcohols..... 2768
Chlorbenzylic alcohol..... 2630
Chlorbutylene hydroxide, *see* Epichlorhydrin.
Chlordextrose pentacetate, *see* Pentacetylchlordextrose.
Chlordextrose tetracetate, *see* Tetracetylchlordextrose.
Chlornaphthalenes 2747
Chlornitronaphthalin 2716
Chlorhydrin 2630
—, solubility cellulose acetate in..... 2608
Chlorhydrins 2735, 2736, 2737, 2806
—, manufacture of..... 2739
—, substituted, plastic of cellulose acetate and..... 2766
Chlorinated acetophenone, *see* Acetophenone, chlorinated.
Chlorinated stearic acid, *see* Stearic acid, chlorinated.
Chlorine, esterifying hydrocellulose in presence of..... 2565
—, manufacture of cellulose formate with..... 2625
Chloroamine 2909
Chlorocitrate emulsion, *see* Emulsion, chlorocitrate.
Chloroform 2720
—, acceleration of acetylation in..... 2539
—, cellulose acetate soluble in..... 2546
—, soluble in alcohol and..... 2583
—, cellulose benzoate solvent..... 2657
—, cellulose esters soluble in..... 2721
—, dissolving acetyl methyl cellulose in..... 2508
—, dissolving ethyl cellulose by..... 2506
—, manufacture of cellulose acetate soluble in...2534, 2561, 2586
—, manufacture from chloral hydrate..... 2730
—, miscibility of acetic acid with..... 2524

Chloroform, properties of 2720
—, starch acetate solvent..... 2935
—, toxicity 2730
Chlorononadeca-acetylerythrodextrin 2645
Chloropropylene oxide, *see* Epichlorhydrin.
Chlorosulfonates 2614
Chlorosulfonic acid.....2589, 2603, 2613
—, formylation in presence of..... 2626
Chlorous anhydride..... 2527
Chlorpalmitic acid..... 2630
Chlorphenetol 2671
Chlorphenol ethers..... 2768
p-Chlorsulfamid 2714
Chlortoluene 2728
Chlortriphenyl phosphate..... 2682
Chromates, dissolving cellulose formate with..... 2632
Chrome alum.....2863, 2870
Chromic acid..... 2831
Chromium, manufacture acetic acid with aldehyde and compounds of..... 2522
Chrono-photography 2864, 2876
Chrysarobin tetra-acetate..... 2692
Chrysarobin triacetate..... 2692
Chrysoidine, dyeing cellulose acetate with..... 2836, 2837
Chrysophenine G..... 2842
Cibal, dyeing cellulose acetate with..... 2841
Cigar tips, coating, cellulose acetate for..... 2887
Cigars, aroma, preserving by cellulose acetate..... 2887
—, bouquet, preserving, cellulose acetate for..... 2887
—, coating with cellulose acetate..... 2887
—, coating with cellulose esters..... 2887
Cinematograph films, *see* Films, photographic.
Cineol 2538
Cineol acetate..... 2538
Cinnamic alcohol, *see* Styrone.
Cinnamic aldehyde, *see also* Oil of cinnamon.
—, ...2704, 2828, 2893
Cinnamyl benzoate..... 2692
Cinnamyl cinnamate..... 2708
Cinnamyl compounds..... 2714
Cinnyl, *see* Cinnamyl.
Citric acid.....2682, 2858, 2859
—, hydrating cellulose esters with..... 2576
Citric ether, *see* Ethyl citrate.
Cleanser, carbon tetrachloride for..... 2724
Cloth, *see also* Cellulose, Cotton, Paper, Wood.
—, acetation of, superficial..... 2555
—, coating, cellulose acetate for.....2807, 2811, 2885
—, damask effect on, producing..... 2561
—, gloss to, imparting..... 2555
—, superficial, acetation..... 2555
—, waxed, cellulose acetate for.....2810, 2901
Clove oil.....2704, 2828
Coal, producing acetic acid from..... 2907
Coca bola wood, imitating by lacquer..... 2799
Coffee husks, manufacture acetic acid from.....2521, 2907

Collapsible tubes, lacquering, cellulose acetate for..... 2798
Collars, celluloid, reinforcing with cellulose acetate..... 2900
—, washable, cellulose acetate for.....2805, 2887, 2900
Collidine 2703
Collodion, *see* Cellulose nitrate.
Collodion, insulating wire with.....2849, 2851
—, protecting cigar tips with..... 2888
Collodion cotton, *see* Cellulose nitrate.
Collodion substitute.....2888, 2889
Colloxylin, *see* Cellulose nitrate.
Colophene 2707
Colophony 2800
—, casein plastic with..... 2772
Color photography, *see* Photography, color.
Colored lacquers, acetate..... 2797
Colors, fixation on textiles, cellulose acetate for..... 2787
—, printing, cellulose acetate for..... 2785
"Comets" (in films) testing for..... 2874
Composition, printing, cellulose acetate for..... 2667
Condensates, *see* Condensation products.
Condensation products.....2771, 2772
—, bleaching 2773
—, phenol-formaldehyde 2766
—, printing on textiles with cellulose acetate and..... 2787
Conductors, electric, insulating, cellulose formate for..... 2633
Confectionery, manufacture, starch acetate for..... 2895
Congo red..... 2832
Constancy (of films), testing..... 2873
Containers, waterproof, manufacture, Cellit for..... 2778
Continuous picture films, *see* Films, picture continuous.
Copaiba 2888
Copal, *see also* Resins.
Copal 2795, 2800
—, aeroplane lacquer of cellulose acetate and..... 2883
—, dichlorethylene solvent of..... 2726
—, estimation of..... 2924
—, lacquers of cellulose acetate and..... 2794
—, solvents for..... 2791
—, tetrachlorethane solvent of..... 2744
—, trichlorethylene solvent for..... 2731
—, wool oil solvent for..... 2719
Copal lacquers..... 2796
Copper, action trichlorethylene on..... 2731
Copper, imitating by lacquer..... 2797
Copper acetate..... 2596
—, anti-fouling composition containing..... 2731
Copper chloride..... 2596
Copper nitrate..... 2596
"Copper number," determining..... 2920
Copper sulfate.....2596, 2951, 2952, 2953, 2954
—, antifouling lacquer containing..... 2731
—, catalyst 2933, 2935
—, manufacture formic acid with..... 2517
Copper (ic), *see also* Copper.
Copper (ic) chloride.....2674, 2957
—, acetylating cellulose with..... 2582

Copper (ic) chloride, dissolving cellulose formate with..... 2632
Copper (ic), sulfate..... 2597
—, acetation with..... 2538
—, dehydrating acetic acid with..... 2523
Copper (ous) chloride, denitrating with..... 2649
Corns, softening, cellulose acetate for..... 2889
Cordite 2846
Corn starch, *see* Starch, corn.
Corset stays, coating, cellulose acetate for.....2798, 2799
—, tips of, coating..... 2799
Cosmetics, cellulose acetate for..... 2889
Cotton, *see also* Cellulose, Paper, Wood.
—, ... 2503
—, absorbent, preparing..... 2504
—, acetation, details of.....2567, 2568, 2569, 2570, 2571
—, —, incomplete 2843
—, —, superficial 2843
—, acetation without change in form..... 2559
—, acetation without solution..... 2796
—, action hydrofluoric acid on..... 2615
—, action acetic anhydride on..... 2528
—, alkylation 2897
—, benzoylation 2656
—, bleaching 2503
—, —, degree of, determination of..... 2503
—, —, peroxide for..... 2503
—, degreasing 2503
—, dyeing before acetation..... 2841
—, formylation of.....2620, 2626
—, gloss, imparting..... 2555
—, impregnating with cellulose acetate..... 2855
—, insulating conductors with cellulose acetate and..... 2847
—, insulating with 2849
—, manufacture oxycellulose from..... 2537
—, Massasoit, acetation of..... 2569
—, preparation of, for acetation..... 2554
—, scouring 2503
—, selection of..... 2503
—, waste, acetation of..... 2505
Cottonseed hulls, obtaining cellulose from..... 2502
Coumarone 2956
p-Coumarone 2956
—, polymerization of..... 2904
Coumarone resin.....2904, 2956
Cravats, cellulose acetate plastic for..... 2772
Creosote 2630
—, cellulose acetate lacquer containing..... 2748
—, manufacture plastic with cellulose acetate and..... 2784
Creosote carbonate..... 2810
Creosote oleate..... 2810
Creosote phosphate..... 2810
Cresol 2714, 2761
—, combining, cellulose acetate, casein and..... 2861
—, cellulose acetate filaments containing..... 2819
Cresol acetates..... 2695
Cresol-formaldehyde condensations..... 2747

Cresols 2668, 2694
—, carbonic esters of 2688
—, dissolving ethyl cellulose by 2506
Cresyl acetate 2692
m-Cresyl butyrate 2694
m-Cresyl isovalerate 2694
Cresyl phosphate 2684
Cresyl phosphoric acid 2682
Cresyl thiophosphate 2684
Cresylic ether 2768
Crystal green 2832
Cuffs, celluloid, reinforcing with cellulose acetate 2900
—, washable, cellulose acetate for 2887
—, waterproofing, cellulose acetate for 2805, 2900
Cumene 2704, 2756
Cuprammonium cellulose, *see* Cellulose cuprammonium.
Cuprous oxide 2548
Cuts, cellulose acetate for 2889
Cyanides, recovery of silver in film by 2876
Cyanogen, acetation of 2530
Cyclohexanol 2669, 2691, 2715
Cyclohexanol acetate 2716, 2797
Cyclohexanol formate 2716, 2797
Cyclohexanone 2679, 2715, 2760
—, increasing solubility cellulose acetate by 2955
Cyclopentanol 2669, 2691
Cyclopentanol acetate 2716
Cyclopentanol esters 2797
Cyclopropane mercaptals 2902
Cyclopropane mercaptans 2902
Cyclopropane polysulfides 2902
Cyclopropane sulfides 2902
Cyclopropane sulfinic acid 2902
Cyclopropane sulfones 2902
Cyclopropane sulfonic acid 2902
Cyclopropane sulfoxides 2902
Cylinder records, cellulose acetate 2879
Cylinders, drying protection from erosion 2540
—, phonograph, see Phonograph cylinders.
Cymene 2707
b-Cymophenol, *see* Carvacrol.

Damask effect, cellulose acetate for producing 2786
Damask effect on textiles, cellulose acetate for 2788
Dammar, *see also* Resin.
—, ... 2795, 2802
—, aeroplane lacquer of cellulose acetate and 2883
—, dichlorethylene solvent of 2726
—, solvents for 2791
—, tetrachlorethane solvent of 2744
—, wood oil solvent for 2719
Dark room filter, cellulose acetate for 2860
De-esterification, *see* Saponification.
Detergine 2721

Dextrin 2643, 2713
—, acetating 2648
—, formylating 2648
Dextrin acetate 2939
Dextrin acetates 2511, 2514
Dextrin acetosulfuric acids 2949
Dextrin dichloracetate 2647
Dextrin formate 2642
Dextrin pentacetate 2514
Dextrins, isolation of 2511
Dextrose, *same as* Glucose.
Dextrose 2501, 2643
—, acetating 2615
—, acetosulfates of 2511
—, acetylation of 2515
—, acetyl derivatives of 2533
—, hydrolysis of cellulose to 2515
Dextrose acetate 2515, 2615
Dextrose pentacetate, *see also* Pentacetyldextrose.
α-Dextrose pentacetate 2513
Dextrose *α*-pentacetate 2516
Dextrose tetracetate 2644
Diacetate of dulcite, *see* Dulcite diacetate.
Diacetic cellulose, *see* Cellulose diacetate.
Diacetin, *see* Glyceryl diacetate.
Di-acetochlorhydrin 2704
Diacetone alcohol 2630, 2717
—, manufacture, Crockett apparatus 2717
—, —, Doerflinger process 2717
—, —, Hoffmann process 2717
—, properties of 2718
—, solubility 2718
Diacetonamine 2717
Diacetonyl alcohol, *see* Diacetone alcohol.
Diacetyltartaric acid esters, solubility cellulose acetate in 2608
Diacetyltartrates, solubility cellulose acetate in 2608
Diamidotoluenes 2706
o-Diamines, chlorinated 2705
o-Diamines, brominated 2705
p-Diaminodiphenyl, *see* Benzidine.
Dianisidin 2702, 2711
—, diazotization of 2839
—, impregnating cellulose acetate with 2837
Diastase 2941
Dibenzenesulfo-*p*-cresol 2714
Dibenzenesulfo-2.7-dioxynaphthalin 2714
Dibenzoylstyrene, action acetic anhydride on 2534
Dibenzylbenzenesulfamid 2714
Dibenzylcatechol 2671
Dibenzyl-*p*-chlorbenzenesulfanilid 2714
Dibenzyl ether 2671
Dibenzylidene acetone 2709
Dibenzyl quinol 2671
Dibenzylresorcinol 2671
Dibenzyl-*p*-toluenesulfanilid 2714
Dichloracetic acid 2600, 2646

Dichloracetone 2679
Dichloracetylchloride 2734
Dichloracetylene 2732, 2733
Dichloraldehyde 2739
2-4-Dichloraniline 2909
Dichlorbenzene 2683, 2772
o-Dichlorbenzene 2728
Dichlorbenzidine 2711
Dichlorcresol 2682
Dichlordiphenyl thiophosphate 2683
Dichlorether 2670
Dichlorethoxyethylene 2728
Dichlorcresol phosphate 2682
Dichlorethylene 2704, 2725, 2740, 2762, 2772, 2795, 2842
—, alcohol and 2762
—, cellulose acetate solvent 2664
—, density 2726
—, emulsifying 2728
—, fractionation 2726
—, lacquers on cellulose acetate and 2727
—, manufacture 2725, 2727
—, plastic of cellulose acetate and 2728
—, properties 2726
—, solubility 2726
—, solvent of alcohol and 2727
—, solvent of epichlorhydrin and 2727
—, testing 2728
—, uninflammable lacquers with 2720
cis-Dichlorethylene 2720
sym-Dichlorethylene 2725, 2739
Dichlorhydrin ..2558, 2562, 2634, 2635, 2689, 2690, 2735, 2736, 2737, 2826, 2840, 2885, 2958
a-Dichlorhydrin 2735
b-Dichlorhydrin 2735
Dichlorhydrin, dissolving ethyl cellulose by 2506
—, dissolving hydrated cellulose acetate in 2576
Dichlorisopropyl alcohols, *see* Chlorhydrins.
Dichlornaphthol 2682
Dichlornaphthol phosphate 2682
Dichlornitronaphthalin 2716
Dichlorobenzene 2731
Dichlorovinyl ether 2729
Dichlorphenetol 2671
Dichlorphenol 2682
Dichlorphenol phosphate 2682
Dichlorphenols 2768
Dichlorpropyl alcohol 2738
Dichlorvinyl ether 2734
Dicresyl carbonate 2683
Dicresylglyceryl ether 2689, 2690
Dicresyl phosphoric acid anilid 2682
Die forms, manufacture cellulose acetate for 2765
Diethylamine 2698
Diethylamine chloride 2580, 2597
Diethylamine sulfate 2597
—, catalytic action of 2541

Diethylaniline 2699
Diethylbarbituric acid 2697
Diethyldiphenyl urea 2697, 2698, 2826
5-Diethyldiphenyl urea 2716
as-Diethyldiphenyl urea 2716
Diethyl ether, *see* Ether, diethyl.
Diethylmalonyl urea 2697
Diethyl phthalate 2690
Diethylpyrocatechin ether 2768
Diethyl sulfate 2507
—, ethylation with 2506
—, manufacture 2593, 2900
Differential dyeing 2836
Diformin, *see* Glyceryl diformate.
Diglucose octacetate, *see* Octacetyldiglucose.
Diglyceryl benzoate 2899
Diglyceryl naphthoate 2899
Diglycose 2604
Dihydric carbocyclic alcoholic esters 2692
Dihydroxybenzene benzyl ethers 2671
Dihydroxydinaphthyl ketone 2712
Dihydroxydiphenyldimethylmethane 2680, 2767, 2904
Dihydroxydiphenylsulphone 2710
Diisobutyl ketone 2677
Diluents, *see* Nitro benzene, Benzene, Water, Alcohol, etc.
Dimethyl-*l*-acetone 2678
Dimethylamine hydrochloride 2598
Dimethylamine sulfate, acetation with 2538
Dimethylaniline 2661, 2699, 2773
Dimethyl ether 2670
Dimethyl-glucose 2898
Dimethyl ketone, *see* Acetone.
Dimethyl sulfate 2593, 2650, 2930
Dinaphthyl 2712
a-Dinaphthyl 2712
b-Dinaphthyl 2712
Dinaphthyl carbonate 2683
Dinaphthyl ketone 2712
Dinaphthylmethane 2712
Dinaphthyl phosphoric acid anilid 2682
Dinitroacetin glycerol 2902
Dinitrobenzene 2846
Dinitrocellulose 2888
Dinitrotoluene 2902
Dinitrotoluol 2715
Dinitroxylol 2715
Dioxydiphenylmethane 2714
Diphenylamine 2684, 2699
Diphenylcarbinol 2669
Diphenylcarbonate 2683
Diphenyl ester 2671, 2768
Diphenyl glyceryl ether 2689, 2690
Diphenylmethane 2698
Diphenyl phosphoric acid anilid 2682
Diphenyl urea 2879
Dip lacquer, cellulose acetate 2781, 2794

Di-*p*-sulfo-2, 7-dioxynaphthalin 2714
Disaccharide 2898
Disalicylic aldehyde 2538
Disc records, cellulose acetate 2879
Discs, manufacture, cellulose acetate plastic for 2770
Disodium phosphate 2933
Diterebene 2707
Di-thiopyroglycide 2902
Documents, lacquering 2795
—, —, cellulose acetate for 2816
—, preserving, cellulose acetate for 2816
Drying cylinders, protection from erosion 2540
Dulcite diacetate 2615
Dulcite triacetate 2615
Duplicating sound record, *see* Phonograph record.
"Dust" (in films), testing for 2874
Dyeing 2835
—, cellulose acetate, nitranilin red for 2839
—, differential 2842
Dyestuffs, absorption of, by cellulose acetate 2546
—, absorption power of, increasing 2837
—, dissolving 2797
—, dyeing cellulose acetate with 2836
—, solvents for 2797

Ears, artificial, manufacture, cellulose acetate for 2900
Earth-nut cake, plastic of cellulose acetate and 2774
Earths, attaching to fabric, cellulose acetate for 2812
Ebony, imitating by lacquer 2799
Elasticity (in films), testing 2875
Electrical insulation, cellulose acetate for 2801
Electric conductors, insulating, cellulose formate for 2633
—, insulating with, cellulose acetate for 2847
Electric construction, acetate lacquer for 2853
Elemi, *see also* Resins.
—, dichlorethylene solvent of 2726
—, solvent for 2791
—, trichlorethylene solvent for 2731
Elephant, imitating hide of 2808
Elongation, cellulose acetate, determining 2919
Elongation (of films), testing 2873
Emaillit 2806, 2885
Embroideries, cellulose acetate for manufacture of 2827
Embroidery, cellulose acetate for 2829
—, strengthening, cellulose acetate for 2834
Empyreumatic oil of juniper, *see* Cade, oil of.
Emulsifier, carbon tetrachloride as 2724
Emulsion, adhesion of (to film), testing 2873
—, chlorocitrate, cellulose acetate in 2858, 2859
—, photographic, cellulose acetate 2667, 2765
—, —, cellulose acetate, Lederer formula 2859
—, print out, cellulose acetate for 2858
—, sensitiveness, testing for 2874
Emulsion (in films), evenness, testing for 2874
—, cleaning, tetrachlorethane in 2750

Emulsion, photographic, backing films for..... 2841
—, —, cellulose acetate for.....2667, 2857
Enamel, insulating wire with..... 2849
Enameled leather, *see* Leather, enameled.
Enamels, sheet steel, resistance of acetic acid to..... 2523
Enamels, white 2798
Engraved plates, *see* Plates, engraved.
Engravings, preserving with cellulose acetate..... 2816
Epichlorhydrin .2558, 2562, 2630, 2634, 2654, 2689, 2704, 2727, 2735, 2774, 2781, 2857
—, dissolving ethyl cellulose by..... 2506
—, dissolving hydrated cellulose acetate in..... 2576
—, manufacture, cellulose acetate soluble in.....2534, 2561
—, manufacture of..... 2738
—, properties 2738
Epididormin 2690
Erica, dyeing cellulose acetate with..... 2836
Ericin, *see* Mesotan.
Erythrodextrin 2645, 2646
Erythrol 2693
Erythrol tetracetate.....2662, 2693
Erythrosine 2860
Essence niobe, *see* Methyl benzoate.
Essential oils..... 2704
Esterification, *see* Cellulose acetation, formylation, etc.
—, components of..... 2501
Etched plates, *see* Plates, etched.
Ethane, chlorides of..... 2710
—, tetrachlorinated, *see* Tetrachlorethane.
Ethenyltrichloramidin 2706, 2713
Ether, diethyl, acetation of.....2538, 2670
—, —, preparation 2670
—, ethyl, *see* Ethyl ether.
Etherification of cellulose, *see* Cellulose etherification.
Ether, manufacture cellulose acetate insoluble in.....2534, 2561
—, miscibility of acetic acid with..... 2524
—, ordinary, *see* Diethyl ether.
Ethers 2670
Ethyl acetanilid 2704, 2709, 2767
Ethyl acetate.....2529, 2685, 2686, 2707, 2809, 2816, 2824, 2853
—, cellulose acetate plastic with..... 2762
—, dissolving ethyl cellulose by..... 2506
—, dissolving hydrated cellulose acetate in..... 2575
—, hydrocellulose aceto-nitrate solvent..... 2649
—, manufacture cellulose acetate insoluble in.....2534, 2561
—, manufacture cellulose acetate soluble in, 2579, 2583, 2777, 2903, 2904
—, miscibility of acetic acid with..... 2524
—, solubility of partially hydrated cellulose acetate in..... 2575
Ethyl acetoacetate 2708, 2816
Ethyl acetone 2678
Ethyl aceto-*o*-nitrochloranilid 2714
1-Ethylacetylamido-2-nitro-3.4.6-trichlorbenzene 2706
Ethyl alcohol 2662
—, dissolving ethyl cellulose by..... 2506
—, increasing solubility cellulose acetate by..... 2955

Ethyl alcohol, manufacture cellulose acetate insoluble in..... 2534
—, manufacture from sawdust..... 2521
—, miscibility of acetic acid with..... 2524
—, solvent of ethylene chloride and..... 2737
Ethyl *o*-amidosulfobenzoate 2714
Ethyl *m*-amidosulfobenzoate 2714
Ethylaniline 2699
Ethyl benzoate 2548, 2693, 2697
—, cellulose acetate plastic with..... 2771
—, dissolving ethyl cellulose by..... 2506
—, manufacture cellulose acetate soluble in..... 2534
Ethyl butyrate 2697
Ethyl carbanilate 2715
Ethyl-carbonic acid, *see* Propionic acid.
Ethyl-cellulose, *see* Cellulose, ethylated.
Ethyl chloracetate 2693, 2704
Ethyl chloride 2734, 2751, 2903
—, chlorination 2754
—, ethylation with 2507
—, preparing ethyl cellulose by..... 2507
Ethyl chlorstearate 2695, 2711, 2880
Ethyl citrate, dissolving ethyl cellulose by..... 2506
Ethyl diacetyltartrate 2608
Ethyl enanthate, *see* Ethyl oenanthate.
Ethyl ether, dissolving ethyl cellulose by..... 2506
Ethyl hydrogen sulfate..... 2670
Ethyl lactate 2695, 2800
Ethyl methyl ketone, *see* Methyl acetone.
Ethyl monochloracetate 2686
Ethyl myristate 2695
Ethyl-*b*-naphthol, cellulose acetate solvent..... 2666
Ethyl oenanthate 2697
Ethyl palmitate 2695, 2828
Ethyl-phenyl ether 2671, 2728, 2768
Ethyl phthalate 2651, 2695, 2711, 2715, 2769, 2824, 2828
—, dissolving ethyl cellulose by..... 2506
Ethyl propyl ketone 2677
Ethyl sebacate 2697
—, dissolving ethyl cellulose by..... 2506
Ethyl silicate 2688, 2793
Ethyl stearate 2711
Ethyl succinate 2715
—, dissolving ethyl cellulose by..... 2506
Ethyl sulfate, preparing ethyl cellulose by..... 2507
Ethyl *p*-sulfoamidobenzoate 2714
Ethyl-sulfuric acid 2594
—, formylation in presence of..... 2627
—, manufacture cellulose butyrate with..... 2639
Ethyl tartrate 2693, 2771
—, dissolving ethyl cellulose by..... 2506
—, solubility cellulose acetate in.....2607, 2608
Ethyl *p*-toluenesulfamido acetate 2714
Ethyl toluenesulfonate 2781
Ethyl toluidine 2700
Ethyl-*o*-toluidine 2701, 2826
Ethyl-*p*-toluolsulfonamid 2704, 2767

Ethyl valerianate 2697
Ethylaniline 2661, 2700
Ethylation, *see* Cellulose.
—, ... 2505
Ethylbenzoyl-*o*-toluidine 2686, 2694, 2826, 2827
Ethylbenzoyltrichloranilid 2713
sym-Ethylbenzoyltrichloranilid 2710
Ethylene, chlorides of 2719
Ethyleneacetochlorhydrin 2631, 2737
Ethylenechlorhydrin 2630, 2737
Ethylene chloride 2630, 2704, 2737, 2901
—, chlorination 2754
Ethylene dichloride 2739
Ethylene diacetate 2708
Ethylenediamine hydrochloride 2580
Ethylene glycol acetate 2662
Ethylene glycol diacetate 2685, 2688, 2806
Ethylene glycol nitrate 2662
Ethylenetrichloramidine 2710
Ethylene trichloride, dissolving ethyl cellulose by 2506
Ethylethenyltrichloramid 2706
Ethylethenyltrichloramidine 2713
Ethylethenyltrichlor-*o*-phenylenediamine 2714
Ethylidenediacetoacetic ester 2709
Ethylidene chlorides 2901
Ethylidene glycol ethers 2685
Ethylxylidine 2700
Eucalyptol, *see* Cineol.
Eugallol 2692
Eugenol 2893
Euresol 2692
Eurobin 2692
Exalgine 2709
Explosive, cellulose benzoate in 2658
Explosives, *see also* Smokeless powder.
Explosives, cellulose acetate 2846, 2902
—, cellulose benzoate for 2641
—, cellulose butyrate for 2639
—, heat of combustion of, decreasing by cellulose acetate 2846
—, increasing stability of by, cellulose benzoate 2846
—, —, cellulose propionate 2846

Fabric, aeroplane, coating with cellulose acetate 2801
Fabrics, *see also* Textiles.
—, acetation, superficial 2555
—, applying metals to, cellulose acetate for 2812
—, brocaded effect, produced by cellulose acetate 2828
—, cellonated 2886
—, coating, cellulose acetate for 2747
—, compound, cellulose acetate for 2811
—, crushed effect, producing by cellulose acetate 2828
—, fireproofing, cellulose acetate for 2813
—, glazing, cellulose acetate for 2804
—, imparting "silk finish" to 2824
—, impregnating, cellulose acetate for 2884

Fabrics, metallized, cellulose acetate for..... 2812
—, mixed, dyeing, cellulose acetate for..... 2843
—, printing on, cellulose acetate for..... 2828
—, rendering impermeable to Roentgen rays..... 2810
—, treating with Cellon 2886
—, trichlorethylene for covering 2733
—, varnish for, cellulose acetate..... 2956
—, waterproofing, cellulose acetate for, 2695, 2784, 2804, 2805, 2813, 2843, 2900
—, waterproofing with cellulose acetate, Gawlich process.... 2813
Fat, determination of, in cellulose..... 2502
—, extraction of, dichlorethylene for..... 2728
—, —, trichlorethylene for 2728
Fats, trichlorethylene solvent for..... 2731
Fatty acid, halogenized, phonograph record of..... 2880
Feathers, stiffening, cellulose acetate for..... 2815
Feculose 2893, 2939
—, properties of 2897
Fehling's solution, determination degree of bleaching by..... 2503
Felt, stiffening, cellulose acetate for..... 2815
Fenone 2853
Ferments, dissolving gelatin from film by..... 2875
Ferric, *see* Iron (ic).
Ferric chloride, *see* Iron (ic) chloride.
Ferrous, *see* Iron (ous).
Ferrous sulfide, *see* Iron (ous), sulfide.
Fibers, acetating, superficial..... 2843
—, asbestos, *see* Asbestos.
—, animal, imitating with cellulose acetate..... 2815
—, cellulose aceto-nitrate 2649
—, trichlorethylene solutions for covering..... 2733
Filaments, artificial, cellulose acetate, 2667, 2747, 2800, 2811, 2817, 2903, 2904
—, —, —, action of water on..... 2833
—, —, cellulose acetate and cellulose nitrate for..... 2651
—, —, cellulose acetate, Beyer process..... 2820
—, —, —, carbon 2845, 2846
—, —, —, dimensions 2828
—, —, —, dyeing, *see also* Cellulose acetate, dyeing.
—, —, —, dyeing 2832
—, —, —, elongation of 2828
—, —, —, Hofmann process 2822
—, —, —, hydrating 2578, 2584
—, —, —, Lederer process 2820
—, —, —, microchemistry of..... 2831
—, —, —, microscopy of 2830, 2832, 2833
—, —, —, Mork process.....2819, 2820, 2862
—, —, —, optical properties of..... 2831
—, —, —, precipitating 2820
—, —, —, properties of.....2818, 2828, 2830
—, —, —, refraction of 2832
—, —, —, Schneeberger method 2822
—, —, —, strength of.....2828, 2834
—, —, —, testing 2831
—, —, —, yield 2819
—, —, cellulose acetonitrate 2649, 2650

Filaments, artificial, cellulose acetophosphate..... 2822
—, —, cellulose ethers for..... 2508
—, —, cellulose formate.....2520, 2625, 2631, 2633
—, —, —, Sammet process 2824
—, —, cellulose nitrate, properties of..... 2818
—, —, cellulose nitrate and cellulose acetate for.....2651, 2843
—, —, cresol acetates for..... 2695
—, —, cuprammonium 2818
—, —, —, testing 2831
—, —, differentiation of.....2831, 2832
—, —, dyeing, *see* Dyeing.
—, —, elasticity of 2831
—, —, ethyl cellulose for..... 2508
—, —, finishing, acetated starch for..... 2895
—, —, firmness of 2831
—, —, formylation of 2620, 2627
—, —, gelatin, manufacture..... 2957
—, —, —, properties of 2830
—, —, gravity of 2830
—, —, inflammable, decreasing 2651
—, —, insulating with 2849
—, —, manufacture from acetic acid solution of cellulose acetate 2525
—, —, microchemistry of 2831
—, —, oleic acid for..... 2681
—, —, optical properties of..... 2831
—, —, polarization of..... 2832
—, —, printing on, cellulose acetate for..... 2788
—, —, solutions for, manufacture..... 2791
—, —, strengthening 2834
—, —, stenosage of 2834
—, —, ultramicroscopy of 2830
—, —, viscose 2957
—, —, —, properties of 2818
—, carbon, cellulose acetate for..... 2845
—, —, cellulose acetate, decreasing cost of..... 2813
—, coating with cellulose acetate..... 2825
—, iridescent, cellulose acetate..... 2824
Film, *see also* Films.
Film, adhesion of emulsion to, testing..... 2873
—, cellulose acetate, capping bottles with..... 2881
—, —, manufacture 2866
—, —, utilizing 2792
—, —, waterproofing 2869
—, —, waste, utilizing..... 2792
—, cellulose nitrate, manufacture..... 2866
—, elongation, determining..... 2919
—, permeability, determining..... 2919
—, photographic, cellulose acetate, manufacture, Danzer process 2863
—, —, —, —, Lumiere process..... 2863
—, —, constancy of..... 2872
—, —, continuous, cellulose acetate, manufacture, Bonwit process 2869
—, —, —, size 2872
—, —, drying, Thompson process..... 2871

Film, photographic, elasticity 2873
—, —, elongation 2873
—, —, —, testing 2873
—, —, evenness, testing for 2874
—, —, firmness 2873
—, —, "fog," testing for 2874
—, —, Goodwin process 2865
—, —, hygroscopicity 2873
—, —, inflammability, testing 2873
—, —, manufacture 2866
—, —, —, Anthony process 2866
—, —, —, Cossitt process 2866
—, —, —, Edwards process 2866
—, —, —, Goodwin process 2865
—, —, —, Hue process 2866
—, —, —, Lumiere process 2867
—, —, —, Mohr process 2866
—, —, —, Ratignier process 2866
—, —, —, Reichenbach process 2865
—, —, —, Stevens and Lefferts process 2865
—, —, —, Thornton process 2866
—, —, —, Thornton and Rothwell process 2866
—, —, —, Walker process 2866
—, —, "rain" in 2872
—, —, "scratches" in 2872
—, —, shrinkage 2872
—, —, testing 2871, 2872
—, —, thickness of 2872
—, —, uninflammable, manufacture 2867
—, porosity, determining 2919
—, recovery of constituents from 2874, 2875
—, separating gelatin from 2807
—, tensile strength, determining 2919
—, utilizing 2792
—, waste, artificial leather for 2807
—, —, cellulose acetate, utilizing 2792, 2874
—, —, utilizing 2799
—, waterproofing 2869
—, —, Danzer process 2867
Film-cement 2956
Films, cellulose acetate 2761, 2763, 2893
—, —, compound 2899
—, —, continuous, manufacture 2865, 2866, 2867
—, —, decreasing cost of 2813
—, —, formation of 2862
—, —, hydrating 2578, 2584
—, —, manufacture of 2764, 2899, 2902
—, —, —, detaching 2862
—, —, —, Knoll process 2864, 2902
—, —, partial hydrolysis of 2841
—, —, pentachlorethane 2752
—, —, pentachlorethane and acetone for 2762
—, —, plastic, manufacture 2765
—, —, testing 2871
—, cellulose diacetates for 2545
—, cellulose formate 2629

Films, cement for 2956
—, cinematographic, cellit for 2780
—, composite, cellulose acetate 2859
—, compound, cellulose acetate 2899
—, continuous, cellulose acetate, manufacture 2764
—, dichlorethylene and cellulose acetate 2727
—, gelatin, coating with cellulose acetate 2863
—, —, decreaisng inflammability of 2863
—, iridescent, cellulose acetate for 2824
—, photographic, cellulose acetate for 2749
—, —, cellulose acetate and tetrachlorethane for 2764
—, —, cellulose acetate, manufacture 2765
—, —, continuous, cellulose acetate 2864
—, —, —, —, manufacture 2866, 2867
—, —, —, —, —, Lederer process 2764
—, —, manufacture plastic 2765
—, —, resorcinol diacetate for 2692
—, —, waterproofing 2898
—, picture, continuous, coating 2898
—, plastic, cellulose acetate 2761
—, sensitized, cellulose acetate for 2858
—, stripping, chalk as an aid to 2867
—, uninflammable, manufacture, Lederer process 2764
—, viscose, coating with cellulose acetate 2863
—, —, decreasing inflammability of 2863
Fingers, staining, preventing by cellulose acetate 2890
Finishes, textiles, cellulose acetate for 2828
Fire extinguisher, carbon tetrachloride for 2724
Firmness (in films), testing 2873
Fish glue 2803
Flesh split, *see* Skins.
Floor lacquer 2795
Flowers, artificial, manufacture, cellulose acetate for 2827, 2829
"Fog" (in films), testing for 2874
Foil, artificial, cellulose acetate for 2811
—, metal, *see* Metal foil.
Formace 2673
Formal, *see* Methylal.
Formaldehyde 2619, 2672, 2731, 2787, 2870
—, condensing with phenol 2772
—, decreasing solubility of acetated starch by 2895
—, manufacture artificial filaments of gelatin and 2957
—, toughening gelatin with 2765
p-Formaldehyde 2731
Formanilid 2709
—, dissolving cellulose ethers with 2506
—, dissolving ethyl cellulose by 2506
Formalin, *see* Formaldehyde.
Formates, manufacture, Sulzer method 2903
Formic acid 2521, 2566, 2617, 2620, 2641, 2680
—, analysis of 2905
—, —, Aufrecht method 2905
—, —, Franzen method 2906
—, —, gravimetric 2906
—, —, Grossmann method 2905
—, —, Klein method 2905

Formic acid, analysis of, mercuric chloride method..... 2906
—, —, permanganate method..... 2905
—, —, Rupp method..... 2905
—, —, titration method 2905
—, —, volumetric 2905
—, cellulose acetate soluble in..... 2607
—, dissolving cellulose acetate in..... 2821
—, dissolving cellulose formate with.....2520, 2631
—, dissolving ethyl cellulose by..... 2506
—, dissolving starch by..... 2520
—, distillation, rate of..... 2525
—, esterizing with..... 2565
—, estimation, bromometric..... 2906
—, —, Jones method 2905
—, —, permanganate method..... 2906
—, hydrochloric acid in, estimation..... 2907
—, hydrolysis of cellulose acetate with..... 2579
—, impurities in..... 2519
—, manufacture 2516, 2905
—, —, Sulzer method..... 2903
—, manufacture cellulose acetate soluble in..... 2586
—, manufacture from alcohol..... 2519
—, occurrence 2516
—, oxalic acid in, detection..... 2907
—, reactive esterfication velocity of..... 2618
—, solvent action of..... 2519
"Formic acid Ester"..... 2773
Formic ether, *see* Ethyl formate.
Formin, *see* Hexamethylenetetramine.
Formins, *see* Glyceryl formates.
Formins 2688
Forms, manufacture cellulose acetate for..... 2765
Formylated albumen, *see* Albumen, formylated.
Formylated cellulose, *see* Cellulose formate.
Formylated starch, *see* Starch formate.
Formylation, *see also* Esterification.
Formylcellulose, *see* Cellulose formate.
Formyldiphenylamine 2701, 2705
Formylnaphthylamine 2705
Fuchsin 2797, 2810, 2838
—, dyeing, cellulose acetate with..... 2836
Furniture police, tetrachlorethane for..... 2747
Furs, coating with cellulose acetate..... 2815
Fusel oil, photographic film containing..... 2865
—, refined, *see also* Amyl alcohol.
—, substitute, tetrachlorethane as..... 2744

Galactose, acetyl derivatives of..... 2533
Galactose octacetate, *see* Octacetylgalactose.
Galactose pentacetate..... 2533
Gallacetophenon 2709
Gallic acid, glycol ester of..... 2688
Galvano lacs 2801
Gas mantles, *see* Mantles, incandescent.
Gaultheria oil..... 2889

Gaultheria oil, *see also* Methyl salicylate.
Gelatin 2860
—, cellulose acetate plastic containing..... 2748
—, coating with cellulose acetate..... 2813
—, combining cellulose acetate with..... 2901
—, emulsion of cellulose acetate and..... 2765
—, films of, coating with cellulose acetate..... 2863
—, hardening 2788
—, indurating 2788
—, mantle dip containing cellulose acetate and..... 2856
—, peptonating 2875
—, plastic of cellulose acetate and..... 2761
—, recovery of (from film).....2792, 2874, 2875
—, separating from film..... 2807
—, waterproofing 2788
Gelignite 2846
Gilded lace..... 2803
—, manufacture of..... 2804
Gilding medium..... 2801
Glacial acetic acid, *see* Acetic acid, glacial.
Glass, applying metals to, cellulose acetate for..... 2812
—, imitation, cellulose acetate for..... 2899
—, substitute, cellulose acetate for.....2784, 2879
—, flexible, cellulose acetate as..... 2899
Glucose, *same as* Dextrose.
Glucose 2535, 2713
Glucose acetate.....2515, 2615, 2616, 2713
Glucose acetates..... 2615
Glucose butyrate..... 2713
Glucose diacetate..... 2713
Glucose dibutyrate..... 2713
Glucose distearate..... 2713
Glucose ditartrate..... 2713
Glucose pentacetate, *see* Pentacetylglucose.
Glucose stearate..... 2713
Glucose tartrate..... 2713
Glucose tetratartrate..... 2713
Glucosides 2889
Glue 2672, 2803, 2860
—, insulating wire with..... 2849
Glycerine, *see* Glycerol.
Glycerol 2666, 2776
—, esterification of..... 2690
"Glycerol ether-oxide"..... 2881
—, hydrating cellulose esters with..... 2582
—, hydrolyzing cellulose with..... 2565
—, manufacture cellulose acetate insoluble in..... 2561
—, plasticity hydrated cellulose acetate in..... 2575
—, sulfuric acid 2943
Glyceryl benzoate.....2691, 2715
Glyceryl benzoates..... 2899
Glyceryl cinnamate..... 2694
Glyceryl diacetate.....2688, 2689
Glyceryl diformate..... 2690
Glyceryl esters, lacquers of cellulose acetate and..... 2956
Glyceryl formate 2617, 2690

Glyceryl formates 2690
Glyceryl monoacetate 2688
Glyceryl monocinnamate 2692
Glyceryl monoformin 2690
Glyceryl naphthoates 2899
Glyceryl oxalates 2690
Gylceryl phthalate 2691
Glyceryl phthalonate 2691
Glyceryl salicylate 2691, 2692
Glyceryl triacetate, is Acetin.
Glyceryl triformate, *see* Glyceryl formate.
—, 2630, 2651, 2662, 2666, 2685, 2688, 2690, 2714, 2772, 2795, 2806. 2826, 2828, 2840, 2884, 2957
—, solubility cellulose acetate in 2608
Glycogens, chloracetyl 2616
Glycol, cellulose acetate solvent 2666
—, hydrating cellulose esters with 2582
Glycol (ethylidene), esters of, manufacture 2932
Glycol aconitate 2688
Glycol esters, manufacture 2932
Glycol anthranilate 2688
Glycol aspartate 2688
Glycol benzoate 2694
Glycol cinnamate 2694
Glycol diacetate 2662
Glycol diacetates 2828
Glycol gallate 2688
Glycol malate 2688
Glycol malonate 2688
Glycol mandelate 2688
Glycol monosalicylate 2688
Glycol naphthoate 2688
Glycol oxalate 2688
Glycol salicylate 2688
Glycol succinate 2688
Glycol tartrate 2688
Glycol toluate 2688
Glycol phthalate 2688
Glycol vanillate 2688
Glycose 2774
—, plastic of cellulose and 2774
Glycose dibutyrate 2774
Glycose octa-acetate 2774
Glycose pentacetate 2774
Glycose triacetate 2774
Gold, printing of, cellulose acetate for 2788
Gold bronze, metallizing fabrics with 2813
Gold lace, manufacture of 2804
Gold leaf, imitating 2803
—, compositions 2802, 2803
Gold paint 2801
Gold yarns, cellulose acetate for 2825
Golf balls, coating 2799
Grain alcohol, *see* Alcohol, ethyl.
Grain split, *see* Skins.
Graphic arts, cellulose acetate plastics in 2769

Graphite, plastic of cellulose acetate and..... 2768
Guaethol 2670
Guaiacol 2666, 2671
—, combining cellulose acetate, casein and..... 2861
Guanidine 2593, 2697, 2823
Guldberg and Waage, law of..... 2551
Gum arabic, *see* Acacia.
Gum benzoin, *see* Benzoin.
Gum benjamin, *see* Benzoin.
Gum-drops, manufacture, acetated starch for..... 2895
Gutta-percha, artificial leather of cellulose acetate and..... 2809
—, resins, cellulose acetate and..... 2772

Hair, artificial, manufacture imitation foil from..... 2811
—, horse, *see* Horsehair.
Hand decorated leather, *see* Leather, hand decorated.
Hands, artificial, manufacture of, cellulose acetate for..... 2900
Hands, protecting, Cellit for..... 2782
Hats, stiffening, cellulose acetate for..... 2814
Hat trimmings, manufacture of, cellulose acetate for..... 2827
—, strengthening, cellulose acetate for..... 2834
Heavy acetone oil, *see* Acetone oil, heavy.
Helindon 2612, 2628
—, dyeing cellulose acetate with..... 2841
Helindon scarlet S.....2841. 2842
Heliotropine 2890
Hemicellulose, determination of, in cellulose..... 2502
Heptacetylcellobiose 2509
Heptacetylchlorlactose 2616
Heptacetylchlorocellobiose 2509
Heptachloracetylmaltose 2615
Herbarium specimens, preserving, cellulose acetate for..... 2782
Hexacetate of dulcite, *see* Dulcite hexacetate.
Hexacetyl mannit, *see* Mannit hexacetate.
Hexachlorbenzene 2729
—, manufacture of..... 2729
Hexachlorethane, 2574, 2734, 2740, 2741, 2751, 2754, 2853, 2883
—, dissolving cellulose acetate and casein with..... 2778
—, dissolving power of..... 2720
—, lacquer of cellulose acetate and..... 2796
—, manufacture 2742, 2751, 2753
—, —, Michel process 2754
—, manufacture thichlorethylene from..... 2728
—, properties 2755
—, solubility 2755
Hexahydro-*o*-cresol 2715
Hexahydrophenols 2797
Hexahydrothymol, *see* Menthol.
Hexamethyleneamine, *see* Hexamethylenetetramine.
Hexamethylenetetramine 2773
Hexanol acetate 2797
Hexaoxybenzene 2662
Hexaoxybenzene hexacetate 2662
Hexose, pentacetyl 2929
—, unmethylated 2898

Hides, coating with cellulose acetate..... 2814
—, imitating with cellulose acetate..... 2808
—, protecting, cellulose acetate for.....2889, 2890
Hippopotamus, imitating hide of..... 2808
v. Hoehnels paper reagent..... 2831
Horn, artificial, manufacture..... 2668
Horsehair, artificial, manufacture, cellulose acetate for..... 2829
Hulls, cottonseed, *see* Cottonseed hulls.
Hydracellulose, acetylation of..... 2537
Hydrating agents 2682
Hydration 2561
—, details of 2573
—, water required for..... 2571
Hydrazine sulfate 2596
Hydrobenzylketones 2716
Hydrobromic acid, swelling cellulose acetate with..... 2838
Hydrocarbon chlorides 2719
—, properties 2719
Hydrocellulose, *see also* Cellulose.
—, ...2501, 2531, 2541
—, acetating,
2512, 2526, 2536, 2555, 2558, 2560, 2562, 2566, 2775, 2777
—, acetophosphates of 2822
—, benzoylation of 2655
—, composition 2542
—, dyeing before acetation..... 2841
—, esters of 2541
—, formulas 2542
—, formylation of 2623, 2624
—, hygroscopicity of 2514
—, manufacture 2558, 2585, 2606, 2624
—, manufacture formic esters from..... 2620
—, manufacture pyroxylin from..... 2531
—, proparation of 2506
Hydrocellulose acetate, alcohol insoluble, manufacture of.2560, 2775
—, formulas of 2543
—, manufacture of 2585, 2714, 2777
—, —, plastic 2775
—, solvents, alcohol 2664
Hydrocellulose aceto-nitrate 2649
Hydrocellulose acetoprosphate 2822
Hydrocellulose benzoate 2641, 2655
Hydrocellulose brombenzoyl chloride 2544
Hydrocellulose butyrate 2543, 2637
—, formulas of 2543
Hydrocellulose chloracetate 2637
Hydrocellulose chlorbutyrate 2637
Hydrocellulose esters, preparation of..... 2542
Hydrocellulose formate 2623
Hydrocellulose iso-valerate 2543
Hydrocellulose nitrobenzoyl chloride 2544
Hydrocellulose propionate 2543, 2637
Hydrocellulose sebacate 2640
Hydrocellulose toluylchloride 2544
Hydrocellulose valerate 2637
Hydrochloric acid, acetation cellulose in presence of..... 2603

Hydrochloric acid, dissolving cellulose by 2614
—, estimation of, in formic acid 2907
—, hydrating cellulose esters with 2576
—, swelling cellulose acetate with 2838
—, treating cellulose acetate with 2837
"Hydrochlorinated turpene" 2707
Hydrofluoric acid, action on cotton 2615
—, manufacture formic acid with 2517
Hydrogen, permeability of, decreasing with cellulose acetate .. 2882
Hydrogen dioxide, bleaching acetated cellulose with 2611
—, sensitizing photographic emulsions with 2860
Hydrogen peroxide, *see* Hydrogen dioxide.
Hydrogenation 2677
Hydrolysis 2536, 2563
Hydronaphthylketones 2716
Hydrosulfites 2731
Hydrous wool fat, *see* Lanolin.
Hydroxybenzene, *see* Phenol.
4-Hydroxy-2-keto-4-methylpentan 2717
Hydroxylamine 2773
Hydroxylamine sulfate 2596
Hygroscopicity (of films), testing 2873
Hypnone, *see* Acetophenone.
Hypochlorites, bleaching 2731

Icosacetyl erythrodextrin 2645
Imitation leather, *see* Leather, imitation.
Imitation rubber, *see* Rubber, imitation.
Immedial dyestuffs 2628
—, dyeing cellulose acetate with 2841
Impregnating composition, cellulose acetate 2902
Incandescent lamps, *see* Lamps, incandescent.
Incandescent mantles, *see* Mantles, incandescent.
Indanthrene 2612, 2628
—, dyeing cellulose acetate with 2841
Indanthrene R. S. dyestuff 2628
Indene 2956
—, polymerization of 2904
p-Indene 2956
India rubber, synthetic, cellulose acetate for 2901
Indigo, synthesis 2734
Induline 2797, 2838
Inflammability (of films), testing 2873
Ink, printing on cellulose acetate with 2806
Insecticide, carbon tetrachloride for 2724
Instruments, lacquering, cellulose acetate for 2797
Insulating cables, *see* Cables, insulating.
—, cellulose aceto-nitrate for 2650
—, cellulose benzoate for 2641, 2658
—, cellulose formate for 2633
—, cellulose nitrate for 2853
—, collodion for 2851
—, electrically, cellulose acetate for 2801
Iodides, dissolving cellulose formate with 2632
Iodine, acetation of 2530

Iodine, manufacture cellulose acetate with 2590
—, reaction of acetated starch with 2897
Iodine and sulfuric acid 2831
Iodine bromide, estering with 2565
Iodine chloride, esterizing with 2565
Iodine monobromide, esterizing with 2565
—, manufacture cellulose formate with 2625
Iodine monochloride, esterizing with 2565
—, manufacture cellulose formate with 2625
Iodine trichloride 2754
—, esterizing with 2565
—, manufacture cellulose formate with 2625
Iodoform 2889
Iodohydrin diacetate 2689
Iridescent filaments, *see* Filaments, iridescent.
Iron, action trichlorethylene on 2731
Iron (ic) chloride 2597
—, acetation with 2538
—, acetylating benzolacetone in presence of 2513
—, catalyst 2946
—, catalyst in esterification 2957
—, catalytic action of 2541
Iron (ic) sulfate 2597
Iron (ous) sulfate 2597
—, acetation with 2538
—, catalytic action of 2541
—, catalyzer 2933
Iron (ous) sulfide 2526
Iron vitriol, *see* Iron (ous) sulfate.
Isinglass 2860
Isoborneol 2707
Isobornyl acetate 2707, 2885
Isobutyl ketone 2677
Isoeugenol, cellulose nitrate solvent 2666
Isosafrol, cellulose acetate solvent 2666

Jackets, surgical, manufacture 2900
Japanese gold paint 2801
Japanese wood oil, *see* Tung oil.
Japan wax, dissolving ethyl cellulose by 2506
Jasmine flower oil 2690
Jelutong 2731
Jelutong resin 2772
Jet black lacquer, manufacture of 2799
Jewelry, mourning, coating with cellulose acetate 2799
Joints, cellulose acetate plastic for packing 2770
Ju-jubes, manufacture, acetated starch in 2895
Juniper, empyreaumatic oil of, *see* Cade oil of.
Jute, acetic anhyride action on 2533
—, impregnating with cellulose acetate 2855

Katharin 2721
Katigen, dyeing cellulose acetate with 2841
—, dyestuffs 2628

Katigen brilliant green 2841
Kauri 2795
—, solvents for 2791
Ketone solvent 2678
Ketones 2674
—, hydroaromatic 2760
—, plastic of cellulose acetate and 2764
Kinematograph films, *see* Films, continuous.
Koline 2675

Lace, cellulose acetate for 2829
—, dressing, acetated starch for 2895
—, gilded 2803
—, metallized, manufacture of 2803, 2804
—, silvered, manufacture of 2803, 2804
—, strengthening, cellulose acetate for 2834
Lacquer, air-craft, cellulose acetate 2956
—, balloon, cellulose acetate 2956
—, bronze 2804
—, brush, *see* Brush lacquer.
—, cellulose acetate 2747, 2956
—, —, dip 2853
—, —, Koller formula 2795
—, —, Leduc Heitz formula 2806
—, cellulose acetate and phenol 2795
—, cellulose nitrate 2956
—, dip, cellulose acetate 2853
—, floor, *see* Floor lacquer.
—, gilding 2803, 2804
—, resin, *see* Resin lacquer.
—, silvering 2803, 2804
—, trichlorethylene as solvent for 2784
Lacquers, *see* also Bronzing liquids, Lakes, Paints and Varnishes.
—, acetate 2789, 2790
—, —, preserving documents with 2816
—, —, solvents for 2790
—, acetate-resin, manufacture 2791
—, air-craft, cellulose acetate 2885
—, anhydrous, producing 2740
—, black, cellulose acetate for 2799
—, cellulose acetate brush 2764, 2791, 2882, 2883
—, —, black 2799
—, —, clarifying 2791
—, —, colored 2797
—, —, dyestuffs for 2797
—, —, electricity of, increasing 2795
—, —, evaporation of 2794
—, —, —, modifying 2795
—, —, filtration 2791
—, —, formulae for 2782, 2794
—, —, inflammability, reducing 2793
—, —, jet black 2799
—, —, Koller formula 2795
—, —, mat black 2799
—, —, manufacture 2791

Lacquers, cellulose acetate, manufacture, Badische process... 2797
—, —, —, Griesheim-Elektron 2796
—, —, non-solvents for 2789, 2790
—, —, pentachlorethane 2753
—, —, properties 2789, 2790, 2792, 2793
—, —, specific gravity of..... 2792
—, —, viscosity 2792
—, —, wrought black 2799
—, —, and dichlorethylene 2727
—, —, and resin 2704
—, cellulose butyrate for..... 2639
—, cellulose nitrate 2529
—, clarifying 2791
—, colored, dyestuffs for..... 2797
—, dip, cellulose acetate..... 2791
—, estimation of cellulose acetate in..... 2923
—, tetrachlorethane 2704, 2795
Lactic acid 2610, 2682
—, cellulose acetate solvent..... 2696
—, cellulose formate solvent.....2619, 2629
—, dissolving cellulose acetate by..... 2821
—, dissolving cellulose formate with..... 2631
—, esters of 2695
—, —, dissolving cellulose esters by..... 2800
—, hydrating cellulose esters with.....2576, 2582
Lactic acid esters, inducing plasticity by..... 2903
Lactose 2713, 2774
Lactose acetate 2616
Lactose octacetate, *see* Octacetyllactose.
Lactose tartrate 2713
Lakes, *see also* Pigments.
—, attaching to fabric, cellulose acetate for..... 2812
—, production of, with cellulose acetate..... 2560
Lamp black 2799
Lamps, incandescent, filaments, cellulose acetate for..... 2845
Lanolin, dissolving ethyl cellulose by..... 2506
Lead, action trichlorethylene on..... 2731
—, salts of, antifouling paint containing..... 2731
Lead chamber crystals, *see* Nitrosyl sulfate.
Lead ricinoleate 2711
Leather, antique, cellulose acetate for..... 2808
—, artificial, *see* Leather, imitation.
—, —, coloring 2932
—, —, embossing 2808
—, —, manufacture of 2809
—, cementing cellulose acetate for..... 2901
—, coating with cellulose acetate..... 2814
—, enameled, cellulose acetate for..... 2814
—, fat in, determination of..... 2733
—, hand decorated, cellulose acetate for..... 2808
—, imitation, cellulose acetate for,
2784, 2807, 2808, 2811, 2812, 2835, 2885
—, mission, cellulose acetate for..... 2808
—, ornamenting 2814
—, patent, cellulose acetate for..... 2814
—, smootching 2808

Leather, Spanish, cellulose acetate for..... 2808
Legs, artificial, manufacture, cellulose acetate for..... 2900
Lemon oil 2704, 2834
—, miscibility of glacial acetic acid with..... 2524
—, refraction of 2832
Lenigallol 2692
Lenirobin 2692
Levulose 2713, 2774
—, acetyl derivatives of..... 2533
Levulose acetate 2616
Levulose pentacetate 2533
Light acetone oil, *see* Acetone oil, light.
Light filter, dark room, cellulose acetate for..... 2860
Light rays, transforming, cellulose acetate for..... 2863
Lignite, producing acetic acid from..... 2907
Lignocellulose, constitution of..... 2533
Lime, *see* Calcium oxide.
Limestone, *see* Calcium carbonate.
Linalool 2690
Linalyl acetate 2690
Lincrusta, manufacture, cellulose acetate for..... 2902
Linen, damp-proof, cellulose acetate for producing..... 2807
—, dressing, acetated starch for..... 2895
—, glazing 2804
—, starched, cellulose acetate for..... 2676
—, —, cellulose butyrate for..... 2739
—, —, imitating with cellulose acetate..... 2804
—, —, treating with cellulose acetate and trichlorethylene.. 2732
—, —, waterproofing, cellulose acetate for..... 2805
—, —, —, Roggenkaemper process 2805
—, sweat proof, cellulose acetate for..... 2807
—, treating, Zimmer process..... 2804
—, treating with cellulose acetate..... 2804
—, washable, waterproofing, cellulose acetate for..... 2806
—, waterproofing, cellulose nitrate for..... 2806
—, —, Douque process 2806
Linen wrappers, waterproofing, cellulose acetate for..... 2806
Lineol, acetation of..... 2946
Linoleum, cellulose acetate containing..... 2902
—, manufacture, cellulose acetate for..... 2901
Linseed oil, boiled..... 2810
—, dissolving ethyl cellulose by..... 2506
—, lacquers containing cellulose acetate and..... 2794
—, varnish 2883
Liquidamber, *see* Storax.
Liquids, bronzing, *see* Bronzing liquids.
Litharge, removing sulfur from formic acid by..... 2519
Lithium chloride 2859
Lutidene 2703

Magenta, *see* Fuchsine.
Magnesia, *see* Magnesium oxide.
Magnesium acetate 2557, 2562
—, acetating with.....2534, 2549, 2928
Magnesium butyrate 2639, 2640

Magnesium carbonate 2566
Magnesium chloride.....2597, 2690, 2858
Magnesium oxide 2566, 2801
—, neutralizing acetic acid with..... 2614
Magnesium propionate 2635
Magnesium ricinoleate 2711
Magnesium stearate 2888
Magnet coils, insulating with cellulose acetate..... 2847
Mahogany, imitating, lacquer for..... 2799
Maisin 2716
Maize starch, *see* Starch, corn.
Maize, stems, esterification of..... 2504
Malachite green 2838
Malayan camphor, *see* Borneol.
Malic acid 2682
—, glycol ester of..... 2688
Malonic acid, glycol ester of..... 2688
Maltose octacetate, *see* Octacetylmaltose.
Madelic acid, glycol ester of..... 2688
Manganese, manufacture acetic acid with aldehyde and compounds 2522
Manganese acetate, manufacture acetic acid from aldehyde by. 2522
Manganese hydroxide 2905
Manganese (ic) oxide..... 2523
Manganic, *see* Manganese (ic).
Manganous, *see* Manganese (ous).
Mannit hexacetate 2615
Mannitol 2693
Mannitol hexacetate 2693
Mannitol tetracetate 2615
Mannol, *see* Manol.
Manol 2630, 2701, 2732, 2753, 2772, 2958
—, manufacture cellulose acetate plastic with..... 2784
Mantles, incandescent, carbon tetrachloride for..... 2725
—, —, dipping, Hirsch process..... 2856
—, —, —, Plaissetty process 2857
—, —, impregnating, cellulose acetate for.....2525, 2855
—, —, stiffening, cellulose acetate for.....2681, 2856
—, —, toughening, cellulose acetate for.....2664, 2761
Maps, preserving with cellulose acetate..... 2816
Mastic, *see* also Resins.
Mastic, dichlorethylene solvent of..... 2726
—, tetrachlorethane solvent of..... 2744
—, trichlorethylene solvent for..... 2731
—, wood oil solvent for..... 2719
Mat black lacquers, manufacture of..... 2799
Mat effects on textiles, cellulose acetate for..... 2788
Mathematical instruments, lacquering..... 2797
Medical jackets, cellulose acetate for manufacture of..... 2890
—, celluloid for 2890
Menthol 2688
Mercaptals, combining cellulose acetate and..... 2902
Mercaptans 2902
Mercerized cellulose, *see* Cellulose hydrate.
Mercerizing, differential, cellulose acetate in..... 2845
Mercuric, *see* Mercury (ic).

Mercurous, *see* Mercury (ous).
Mercury, anti-fouling paint containing..... 2772
—, salts of, antifouling paint containing..... 2731
Mercury (ic) chloride, manufacture acetic acid from acetylene and 2527
Mesityl oxide 2671, 2680
—, solubility of 2671
Mesotan 2688
Metacetonic acid, *see* Propionic acid.
Metakalin 2787
Metal foil, manufacture, cellulose acetate for..... 2811
Metallic bedsteads, coating..... 2798
Metallic fabrics, *see* Fabrics, metallized.
Metallized lace 2803
Metal plates, chased, cellulose acetate for..... 2899
—, engraved, cellulose acetate for..... 2899
Metal polish, carbon tetrachloride for..... 2725
Metals, action perchlorethylene on..... 2732
—, action trichlorethylene on..... 2731
—, insulating, cellulose acetate for..... 2853
—, lacquering, cellulose acetate for..... 2784
—, printing with, cellulose acetate for....2785, 2786, 2787 2788
—, printing of, cellulose acetate for.....2787, 2788
—, protection, cellulose benzoate for..... 2658
Metantimonates 2793
Metaphosphoric acid, *see* Phosphoric (meta) acid.
Metavanadates 2793
Methane, chlorides of..... 2719
Methenyl-*o*-toluylenediamine 2701, 2706
Methenyl-3.4-toluylenediamine 2701
Methenyl trichloramidin 2706, 2713
p-Methoxypropenylbenzene, *see* Anethol.
p-Methoxybenzaldehyde, *see* Anisic aldehyde.
Methoxyl salicylate, *see* Mesotan.
Methyl acetanilid.....2704, 2709, 2710, 2767, 2781
Methylacetanilid-phenylacetamide 2709
Methyl acetate 2529, 2673, 2685
—, dissolving ethyl cellulose by..... 2506
Methyl acetic acid, *see* Propionic acid.
Methyl acetone 2633, 2677, 2678, 2679
Methylacetyltetrachloranilid 2713
Methylacetyl-*o*-toluidine 2701, 2826
Methylal 2670
Methyl alcohol, cellulose acetate solvent..... 2665
—, dissolving ethyl cellulose by..... 2506
—, manufacture cellulose acetate insoluble in..... 2534
—, manufacture formic acid from..... 2519
—, miscibility of acetic acid with..... 2524
—, solvent of ethylene chloride and..... 2737
Methyl aldehyde 2805
Methylamine 2593, 2697, 2823
Methylamine bisulfate.....2577, 2590, 2595, 2955
Methylamine sulfate,
2577, 2595, 2900, 2933, 2951, 2952, 2953, 2954
—, catalyzer 2933, 2936, 2943
—, hydrating cellulose esters with..... 2581

Methylaminobenzyl alcohol 2708
Methylaniline 2661, 2699, 2705, 2773
Methylated cellulose, *see* Cellulose, methylated.
Methylated ether 2670, 2805
Methylated spirit 2861
Methylation, *see* Cellulose, methylation.
Methyl benzoate 2693
—, cellulose acetate plastic with..... 2771
Methylbenzoyltrichloranilid 2826
sym-Methylbenzoyltrichloranilid 2710
Methylbenzoyltrichloraniline 2699
Methylbenzyltrichloraniline 2699
Methyl blue 2810
Methylbutenylketone, *see* Mesityl oxide.
Methyl carbanilate 2715
Methyl cellulose, *see* Cellulose, methylated.
Methyl chloracetate 2693
Methyl chloride, methylation with..... 2507
—, preparing methyl cellulose with..... 2507
Methyl chlorstearate 2711, 2880
Methylcyclohexanol 2715
Methylcyclohexanol acetate 2797
Methylcyclohexanol formate 2797
o-Methylcyclohexanol formate 2716
l-Methylcyclohexanone 2715
b-Methylcyclopentanol 2797
b-Methylcyclopentanol acetate 2716
Methylene acetone, manufacture..... 2677
Methylene blue.....2797, 2799, 2810, 2838, 2860
Methylene blue, 2B 2832
—, absorption of, by cellulose acetate..... 2546
—, dyeing cellulose acetate with..... 2836
Methylene chloride 2901, 2909
Methylene dimethylether 2670
Methylenedimethylate, *see* Methylal.
Methylene violet 2810
Methylethenyltrichloramidine 2706, 2714
Methyl ethyl ether 2670
Methyl ethyl ketone.....2633, 2745
Methyl formate 2629, 2630, 2685, 2693, 2694
Methyl-glucoses 2698
Methyl-glucosides 2898
Methyl green 2810, 2852
Methylhexanol acetate 2797
Methylhexanol formate 2797
Methylhydroxynaphthyl ketone 2712
Methyl isopropyl ketone.....2677, 2678
Methyl isopropyl phenol, *see* Thymol.
Methyl lactate 2800
Methylmaltoside heptacetate 2616
Methylmethenyltrichloramidine 2713
Methyl monochloracetate 2686
Methyl myristate 2696
Methyl-*α*-naphthol, cellulose acetate solvent..... 2666
Methylnaphthyl ketone 2712
Methyl oxalate 2696

Methyl oxalate, manufacture plastic cellulose acetate films.... 2765
Methyl oxanilate 2683, 2712
Methyloxymethyl salicylate 2688
Methyl palmitate 2696
3-Methyl-5-phenyl-4-6-dicarboxyethyl-keto-R-hexen 2708
Methyl-phenyl ether 2671, 2728, 2768,2769
—, cellulose acetate plastic with..... 2771
Methyl phenyl ketone 2679
Methyl phthalate.....2696, 2715, 2769, 2884
—, manufacture plastic cellulose acetic films with..... 2765
Methyl propyl ketone.....2677, 2678
Methyl-*n*-propylphenol, *see* Thymol.
Methyl propylphenyl hexahydride, *see* Menthol.
a-Methyl pyridine, *see* Picoline.
Methyl salicylate 2704
Methyl silicate.....2696, 2688, 2793, 2805
Methyl stearate 2696
Methyl succinate 2715
Methyl sulfate 2903
—, acetylating with 2549
—, methylation of cellulose by..... 2508
—, preparing methyl cellulose by..... 2507
Methyl-*p*-toluenesulfamate 2775
Methyl-*p*-toluenesulfonate 2696
Methyl-*p*-toluidinesulfonate, manufacture cellulose acetate films with 2765
Methyl-*o*-toluylenediamine 2713
Methyl violet 2797, 2838
Mica, plastic of cellulose acetate and..... 2768
—, printing with cellulose acetate and..... 2829
Microscopes, lacquering, cellulose acetate for..... 2797
Milk, analysis, trichlorethylene for..... 2733
Millinery, cellulose acetate films in..... 2772
Mineral oils, *see* also Paraffin, Vaseline, etc.
Mission leather, *see* Leather, mission.
Moire effects, producing, cellulose acetate for..... 2788
Moisture, influence of, in acetation..... 2567
Molybdenum salts 2793
Monoacetic cellulose, *see* Cellulose monoacetate.
Monoacetin, *see* Glyceryl monoacetate.
Monoacetylbenzidine 2711
Monoacetyldianisidine 2711
Monoacetyldichlorbenzidine 2711
Monoacetylethylaniline 2664, 2686
Monoacetyltolidine 2711
Monochloracetic acid 2542, 2600, 2804
—, hydrating cellulose acetate with..... 2576
Monochloracetylene 2732
Monochlorbenzene 2885
p-Monochlorbenzylidine diacetate 2713
Monochlorbenzol, *see* Monochlorbenzene.
Monochlorether 2670
Monochlorhydrin 2689
Monochlorhydrin di-acetate 2689
Monochlorhydrin mono-acetate..... 2689
Monochlornaphthalin 2683

Monochlortriphenyl phosphate 2682
Monoethylacetyltrichloranilid 2713
Monoethylaniline 26661, 2699
Monoethyl phthalate 2711
Monoformin, *see* Glyseryl monoformate.
Monoglyceryl benzoate ..... 2899..
Monoglyceryl naphtoate 2899
Monomethylacetyltrichloranilid 2713
Monomethylaminobenzyl alcohol 2708
Monomethylaniline 2661, 2699
Monoplane wings, *see* Wings, monoplane.
Mono-thiopyroglycide 2902
"Motion pictures" 2876
Motograph 2876
Mourning jewelry, lacquering, cellulose acetate for..... 2799
Moving pictures 2864, 2876
Mucic acid, acetylation of..... 2535
Muriatic acid, *see* Hydrochloric acid.

Naphtha, *see* Benzine.
—, dissolving ethyl cellulose by..... 2506
—, solvent 2756
Naphthalene 2566, 2703, 2767, 2775
—, dissoling ethyl cellulose by..... 2506
—, manufacture plastic cellulose acetate films with..... 2765
—, plastic of cellulose acetate, rosin and..... 2710
Naphthalene-*a*-sulfonic acid 2921
Naphthalene-*b*-sulfonic acid 2921
Naphthalin 2712, 2715, 2756
Naphthalol, *see* Betol.
Naphthas, precipitating cellulose acetate by..... 2820
Naphthionic acid, impregnating cellulose acetate with..... 2837
Naphthoic acid, glycol ester of..... 2688
Naphthol 2714
Naphthol, carbonic esters of..... 2683
—, plastic of cellulose acetate and..... 2763
a-Naphthol 2666, 2669
b-Naphthol 2666,2669, 2883
—, cellulose acetate plastic containing..... 2755
—, diazotization of 2839
—, impregnating cellulose acetate with..... 2837
b-Naphthol benzoate 2693, 2715
b-Naphthol salicylate, see Betol.
Naphthol sulfonic acid..... 2590
Naphthol yellow 2797
—, dyeing cellulose acetate with..... 2836
Naphthosalol, *see* Betol.
Naphthoxylacetic acid esters .....
Naphthyl acetate.....2630, 2696, 2712, 2860, 2958
a-Naphthyl acetate 2712, 2713
b-Naphthyl acetate 2712, 2826
a-Naphthylamine bordeaux, dyeing cellulose acetate with..... 2839
—, impregnating cellulose acetate with..... 2837
b-Naphthylamine 2702
—, impregnating cellulose acetate with..... 2837

a-Naphthylaminedihydrocarvone 2702
Naphthyl benzoate 2712
b-Naphthyl benzoate 2771
a-Naphthyldihydrocarbon 2766
a-Naphthyldihydrocarvone 2679
Naphthyl group 2714
a-Naphthylmethane 2712
b-Naphthylmethane 2712
Naphthyl naphthoxyacetate 2712
Naphthyl naphthoxylacetate 2713
Naphthyl oxanilate 2712
Naphthyl phosphate 2684
Naphthyl phosphoric acid 2682
b-Naphthyl phthalate 2769
Naphthyl thiophosphate 2684
Naphthylic ether 2768
Nettles, formic acid in 2516
Nickel chloride 2858
Nicotine 2708
Nigrosine 2797, 2799, 2884
Nigrosines, basic 2838
N. I. film 2792
Nitranilin red, dyeing cellulose acetate with 2839
Nitroanilines 2699
p-Nitraniline, diazotization of 2839
—, impregnating cellulose acetate with 2837
p-Nitraraniline hydrochloride, dyeing cellulose acetate with ... 2839
Nitration, maximum 2537
Nitric acid, acetylating cellulose in presence of 2603
—, hydrating cellulose acetate with 2576
—, hydration with 2581
—, manufacture oxycellulose with 2567
—, swelling cellulose acetate with 2838
Nitroacetanilid 2709
Nitroanisol 2671
p-Nitroacetoacetanilid 2716
Nitroacetins 2690, 2691
Nitroacettoluide 2709
Nitroacetylcellulose, *see* Acetylnitrocellulose.
o-Nitroacylamido derivatives 2706
Nitroanisoles 2768
Nitrobenzene, 2549, 2557, 2558, 2562, 2563, 2595, 2622, 2630, 2634, 2635, 2640, 2650, 2757, 2761, 2853, 2857, 2865
—, acetation in presence of 2928
—, cellulose benzoate solvent 2657
—, dissolving ethyl cellulose by 2506
—, manufacture cellulose acetate soluble in, ... 2534, 2561, 2565, 2586, 2776
—, solubility hydrated cellulise acetate in 2575
Nitrobenzol, *see* Nitrobenzene.
m-Nitrobenzoyl chloride 2544
Nitrocellulose silk, *see* Filaments, artificial, cellulose nitrate.
Nitrocellulose sulfuric acid esters, *see* Cellulose nitrate, sulfuric acid esters.
Nitrochlorbenzene 2702
Nitrocuminol 2549

Nitrocymene 2707
Nitroformins 2690, 2691
Nitroglycerol brisance of, modifying by cellulose acetate..... 2846
Nitrosyl groups 2714
Nitromethane 2630, 2703
—, dissolving ethyl cellulose by..... 2506
—, solubility cellulose acetate in..... 2608
Nitromethylphenyl ether 2671
Nitronaphthalin 2702, 2716
Nitrophenol 2668
—, plastic of cellulose acetate and..... 2763
Nitrophenols, dissolving ethyl cellulose by..... 2506
Nitrophenyl compounds 2714
Nitrosyl sulfate, acetating cellulose with..... 2586
Nitrotoluene 2563, 2702
—, acetation in process of..... 2923
o-Nitrotoluene 2549, 2701
p-Nitrotoluene 2549, 2715
o-Nitrotoluol, *see* *o*-Nitrotoluene.
p-Nitrotoluol, *see* *p*-Nitrotoluene.
Nitroxycellulose 2947
Nitroxylol 2549
Normal cellulose triacetate, *see* Cellulose triacetate.
Normal triacetates, *see* Cellulose triacetate.
Noses, artificial, manufacture, cellulose acetate for..... 2900

O-acetyl compounds, analysis of..... 2921
Octa-acetylcellobiose, *see* Cellobiose octasetate.
Octacetyldiglucose 2616, 2713
Octacetylgalactose, chlorinated 2616
—, nitrated 2616
Octacetyllactose 2616
—, chlorinated 2616
—, nitrated 2616
Octacetylmaltose 2616
—, chlorinated 216
—, nitrated 2616
Octacetylsaccharose 2616
Octoformylcellobiose, *see* Cellobiose octoformate.
Oilcloth, manufacture, cellulose acetate for..... 2901
Oil of amber, *see* Amber oil.
Oil of bergamont, *see* Bergamont oil.
Oil of bitter almonds, *see* Benzaldehyde.
Oil of cade, *see* Cade oil.
Oil of camphor..... 2728, 2820
—, dissolving ethyl cellulose by..... 2506
—, heavy 2704
—, light 2704
Oil of caraway seed..... 2704
Oil of cedar..... 2704
Oil of celery..... 2704
Oil of cinnamon, *see also* Cinnamic aldehyde.
Oil of cloves, *see* Clove oil.
Oil of cognac, *see* ethyl oenanthate.
Oil of hedeoma, *see* Pennyroyal oil.

Oil of lemon, *see* Lemon oil.
Oil of origanum, *see* Origanum oil.
Oil of pennyroyal, *see* Pennyroyal oil.
Oil of rosemary, *see* Rosemary oil.
Oil of sandal wood, *see* Sandal wood oil.
Oil of thuja, *see* Thuja oil.
Oil, trichlorethylene as solvent for..... 2734
Oil of turpentine 2750
—, dissolving ethyl cellulose by..... 2506
Oils, hydrolyzing cellulose with..... 2565
Oleic acid 2681, 2693
—, cellulose acetate plastic with..... 2771
—, softening cellulose acetate filaments with..... 2819
Oleoptens 2704
Oleum, *see* Sulfuric acid, fuming.
Olive oil, dissolving ethyl cellulose by..... 2506
Organic compounds, acetyl groups in, determining..... 2921
Oriental gold paint..... 2801
Origanum oil 2704
Orthopedic appliances, manufacture cellulose acetate for..... 2900
Orthophosphoric acid, *see* Phosphoric (ortho) acid.
Oxalic acid 2682
—, bleaching cellulose acetate with..... 2612
—, estimation of, in formic acid..... 2907
—, glycol ester of 2688
—, hydrating cellulose esters with..... 2576
—, manufacture formic acid with..... 2517
Oxalic acid esters..... 2826
Oxalins, *see* Glyceryl oxalates.
Oxanilic esters 2712
Oxyacetophenon 2709
Oxyalphyl compounds 2714
p-Oxybenzophenon 2709
Oxycellulose 2501
—, acetation of 2537, 2566
—, acetophosphates of 2822
—, acetylating 2536, 2555, 2559
—, determination of, in cellulose..... 2502
—, dyeing before acetation..... 2841
—, formylation of 2626
—, preparation of 2538, 2567
Oxycellulose acetate 2548
Oxycellulose acetophosphates 2822
p-Oxyethylacetanilid 2709
Oxycymol, *see* Carvacrol.
Oxymethylene 2805
Oxyphenylbenzyl ketone 2709
Oxytrimethylenesulfide 2902

"*P*-2 Solvent" 2673, 2764
Packing joints, cellulose acetate and pulp for..... 2770
Paint, antifouling 2772
Paints, *see also* Lacquers and Varnishes.
—, acid proof 2773
—, bleaching, sulfurous acid for..... 2773

Paints, cellulose acetate, manufacture 2731
Palmitic acid 2566
—, esterizing with 2565
Panes, window, *see* Window panes.
Paper, *see also* Cotton, Cellulose, Wood.
—, applying metals to, cellulose acetate for 2812
—, coating, acetated starch for 2895
—, impregnation, cellulose acetate for 2816
—, —, cellulose acetate and hexachlorethane for 2755
—, impregnating with wood pulp 2855
—, lacquering 2795
—, manufacture oxycellulose from 2537
—, printing, sensitized, cellulose acetate for 2858
—, sensitized, cellulose acetate for 2858
—, sizing of, starch acetate for 2895, 2896
—, tissue, acetation of 2505, 2554, 2568
—, transparent, manufacture, cellulose acetate for 2901
—, waterproofing, cellulose acetate for 2805, 2806
—, waxed, cellulose acetate for 2810
Paper pulp, plastic of cellulose acetate and 2770
Paper reagent v. Hoehnels 2831
Papers, legal, protecting, cellulose acetate for 2817
Paraffin, *see also* Vaseline, Mineral oils, etc.
—, ... 2734, 2856
—, solidifying alcohol by 2890
Paraffin oil, dissolving ethyl cellulose by 2506
Paraformaldehyde, *see also* Formaldehyde.
—, ... 2672
—, condensation, products of 2772
Paratungstates 2793
Parchment, artificial 2532
—, lacquering, cellulose acetate for 2816
Parsley camphor, *see* Apiol.
Passamenterie, strengthening, cellulose acetate for 2834
Pasteboard, waterproofing, cellulose acetate for 2805, 2806
Patchouly 2893
Patent leather, *see* Leather, patent.
Patterns, printing, cellulose acetate for 2786
"Pearl essence" 2903
Pearls, artificial, cellulose acetate for 2903
Pellicle, *see* Film.
Pennyroyal oil 2704, 2715
Pentacetylcellulose 2534
Pentacetylchlordextrose 2616
Pentacetyl dextrose 2513, 2515, 2533, 2616, 2955
—, conversion of cellulose to 2515
Pentacetyl galactose 2533, 2616
Pentacetylglucose 2616, 2644
Pentacetylhexose 2509
Pentacetyl levulose 2533, 2713
Pentaethyl cellulose 2507
Pentachlorethane, 2574, 2630, 2661, 2676, 2721, 2734, 2739, 2741, 2741, 2748, 2751, 2762, 2795, 2826, 2899
—, cellulose acetate solvent 2664
—, —, of acetone and 2762
—, —, of alcohol and 2762

Pentachlorethane, dissolving cellulose acetate and casein with. 2773
—, dissolving ethyl cellulose by..... 2506
—, manufacture 2751, 2752
—, —, by ultraviolet rays..... 2753
—, properties 2752
—, solubility 2752
—, —, cellulose acetate in..... 2574
—, —, cellulose propionate in..... 2638
—, uses 2753, 2754
Pentachlornaphthalene 2747
Peppermint camphor, *see* Menthol.
Perborates, bleaching 2731
Percarbonates, bleaching 2731
Perchorethane, *see* Hexachlorethane.
Perchlorethylene 2667, 2732, 2733, 2734, 2795, 2903
—, action of, on metals..... 2732
—, cellulose acetate solvent with phenol..... 2735
—, dissolving cellulose acetate and casein with..... 2773
—, manufacture of 2734, 2735
—, —, Bourgoin process 2735
—, —, Combes process 2735
—, —, Geuther process 2735
—, properties 2735
—, uninflammable lacquer with..... 2720
Perchloric acid, acetation with.....2538, 2539
Permeability, cellulose acetate, determining..... 2919
Peroxide, bleaching cotton with..... 2503
Peroxides, bleaching 2731
Persulfates, bleaching 2731
Peru balsam 2692, 2708, 2888, 2893
Pepsin, dissolving gelatin from film by..... 2875
Petroleum, acetation in..... 2566
—, decreasing inflammability of cellulose acetate with..... 2608
—, dissolving ethyl cellulose by..... 2506
—, hydrolyzing cellulose with..... 2565
Petroleum ether, *see* Benzine.
Petroleum oil, light, *see* Benzine.
Petroleum spirit, recovery of acetic anhydride by..... 2613
Pharmacy, acetated cellulose in.....2534, 2888
Phenacetin 2709
Phenetol, *see* Ethyl phenyl ether.
Phenol...2557, 2566, 2667, 2714, 2733, 2761, 2787, 2901, 2903
—, carbonic esters of..... 2683
—, cellulose acetate filaments containing..... 2819
—, cellulose acetate lacquer containing..... 2795
—, cellulose acetate solvent with perchlorethylene..... 2735
—, cellulose benzoate solvent..... 2657
—, combining casein, cellulose acetate and..... 2861
—, combining cellulose acetate, trichlorethylene and..... 2903
—, dissolving ethyl cellulose by..... 2506
—, hydrating cellulose esters with..... 2582
—, manufacture cellulose acetate soluble in.....2546, 2586
—, plastic of casein, cellulose acetate and..... 2766
—, plastics, manufacture with cellulose acetate..... 2765
—, plastics of cellulose acetate and.....2667, 2763, 2700
—, solvent 2747

Phenol sulfonate 2696
Phenolsulphonic acid 2541, 2590
Phenol-aldehydes, *see also* Condensation products.
—, condensations of 2672, 2731
Phenol esters 2810
Phenol-formaldehyde, condensation products of 2766
Phenolic compounds, plastics of cellulose acetate and 2761
Phenols, polyhydric 2733
Phenoxyacetic ester 2826
Phenoxyacetic ether, *see* Phenyl acetate.
Phenyl 2714
Phenyl acetate 2661, 2685, 2691
Phenylallyl alcohol, *see* Styrone.
Phenylalkylamines 2699
Phenylamine, *see* Aniline.
Phenylaminobenzyl alcohol 2708
Phenylbenzyl ketone 2709
Phenyl cellulose 2657
Phenyl citrate 2713
Phenylcresyl phosphate 2682
Phenylhydrazine 2937
m-Phenylenediamin, impregnating cellulose acetate 2837
Phenyl ether, dissolving ethyl cellulose by 2506
Phenyl ethers 2671
Phenyl formate 2713
Phenylglycide 2689, 2690
Phenylglycin 2734
Phenylglycin ester 2734
Phenyl isocyanide 2700
Phenylnaphthalin 2712
a-Phenylnaphthalin 2712
b-Phenylnaphthalin 2712
Phenyl naphthoxyacetate 2712
Phenyloxylacetic acid 2712, 2713
Phenyloxylacetic acid esters 2713
Phenyl oxide, *see* Diphenyl ether.
Phenyl phosphate 2684, 2715
Phenyl phosphoric acid 2682
Phenyl propionate 2713
Phenylpropyl cinnamate 2708
Phenyl salicylate 2684
Phenyl sulfocyanate 2700
Phenyl tartrate 2713
Phenyl thiophosphate 2684
Philosophical instruments, lacquering, cellulose acetate for ... 2797
Phoenixin 2721
Phonograph cylinders, cellulose acetate and chlorinated stearic acid for 2676
Phonograph records, cellulose acetate 2879, 2902
—, —, manufacture, Aylesworth process 2880
—, —, —, Lumiere process 2880
—, manufacture, cellulose acetate for 2749
—, protecting, cellulose acetate for 2902
Phonography, cellulose acetate in 2879
Phosgene, *see* Carbonyl chloride.
Phosphoric acid 2650

Phosphoric acid, acetation with..... 2538
—, dissolving cellulose formate by..... 2631
—, hydrating cellulose esters with..... 2576
—, manufacture formic acid with..... 2518
—, purification of acetic acid with..... 2522
Phosphoric (meta) acid, acetation with..... 2566
Phosphoric (ortho) acid, acetation with.....2539, 2566
Phosphoric (pyro) acid, acetation with.....2566, 2586, 2822
Phosphoric anhydride, *see* Phosphorus pentoxide.
Phosphoric oxide, *see* Phosphorus pentoxide.
Phosphorus, trichlorethylene solvent for..... 2731
Phosphorus chloride, *see* Phosphorus tri- and penta-chloride.
Phosphorus oxychloride..... 2601
Phosphorus pentachloride 2601, 2738, 2751
Phosphorus pentoxide, acetation with.....2539, 2566
—, nitration in presence of..... 2945
Phosphorus trichloride, acetation with..... 2538
Photographic emulsions, *see* Emulsions, photographic.
Photographic film, waste, utilizing..... 2799
Photographic papers coating..... 2816
Photography, cellulose acetate in..... 2857
—, color, bleach out process, cellulose acetate in..... 2859
—, —, cellulose acetate in.....2859, 2860
—, films for, *see* Films.
—, lacquering in 2795
Photography, roll film..... 2864
Phthalamic acid 2711
Phthalamic anhydride 2711
Phthalanic acid 2711
Phthalanilic anhydride 2711
Phthalic acid 2711
—, cellulose acetate plastic with..... 2771
—, glyceryl esters of..... 2691
—, glycol ester of..... 2688
Phthalic acid esters.....2824, 2826
Phthalic anhydride 2711
Phthalic ether, *see* Ethyl phthalate.
Phthalimide 2702, 2826
Phthalonic acid 2711
—, glyceryl esters of..... 2691
Phthalonic anhydride 2711
Picoline 2703
—, dissolving ethyl cellulose by..... 2506
Picture, motion, developing.....2778, 2879
—, —, drying 2879
—, —, inspecting 2879
—, —, printing 2879
Piece goods, printing, cellulose acetate in..... 2828
Pigments, *see also* Lakes.
Pigment colors, printing, cellulose acetate for..... 2785
Pigments, fixation on textiles, cellulose acetate for..... 2787
Pine needles, formic acid in..... 2516
Pinene 2750
Pinene hydrochloride..... 2707
Pipes, lacquering, cellulose acetate for..... 2794
Pitch, waterproofing wood with..... 2854

Plastic, cellulose acetate and hexachlorethane..... 2755
Plasticity 2575
Plastics, *see also* Solvents.
—, camphor-containing, analysis of..... 2923
—, cellulose acetate, *see* Cellulose acetate, plastics.
—, —, ... 2748
—, —, Lehmann process..... 2903
—, —, manufacture 2958
—, —, pentachlorethane for 2753
—, cellulose acetate and epichlorhydrin..... 2738
—, cellulose acetate and trichlorethylene..... 2732
Plastics, cellulose ethers for..... 2509
—, phenol 2761
Plastol 2714
Plates, chased, imitation, cellulose acetate for..... 2899
—, engraved, cellulose acetate in producing..... 2743
—, etched, reproducing, cellulose acetate for..... 2763
—, metal, engraved, imitation, cellulose acetate for..... 2899
—, sensitized, cellulose acetate for..... 2858
Polka dots, printing, cellulose acetate for..... 2786
Polychloramidines 2713
Polychloranilines 2713
Polyphenylamines 2699
Polysulfides, combining cellulose acetate with..... 2902
Polysaccharides 2501, 2538
Ponceau 4 GE, dyeing cellulose acetate with..... 2837
Poplar wood, acetating..... 2568
Poppyseed oil, varnish 2883
Porosity, cellulose acetate, determining..... 2919
Potassium acetate 2520, 2593
—, ant-acid in acetation 2823
Potassium acid sulfate.....2951, 2952, 2953, 2954
Potassium bisulfate 2933
—, catalyzer 2938
Potassium chlorate, manufacture oxycellulose with.....2538, 2567
Potassium hydroxide, saponifying cellulose acetate by..... 2585
Potassium margarate 2881
Potassium metantimonate 2793
Potassium metavanadate 2793
Potassium oleate 2881
Potassium palmitate 2881
Potassium paratungstate 2793
Potassium permanganate 2674
—, bleaching cellulose acetate with..... 2612
—, purification of acetic acid with..... 2522
Potassium stearate 2881
Potassium sulfocyanides, cellulose acetate solvent.....2622, 2665
Potato starch, *see* Starch.
Powder, smokeless, *see* Smokeless powder.
Preserving documents, cellulose acetate for..... 2816
Printing, cellulose acetate for..... 2903
—, cellulose acetate plastics in..... 2769
—, calico, thickeners for..... 2785
Printing composition, cellulose acetate for..... 2667
Printing forms, manufacture, cellulose acetate for..... 2765
Printing on textiles, cellulose acetate for..... 2786

Printing on textiles, formula for 2787
—, Sericose for 2787
Printing plates, cellulose acetate for 2899
Prints, textile, cellulose acetate for 2787
Propane mercaptals 2902
Propane mercaptans 2902
Propane sulfides 2902
Propane sulfinic acid 2902
Propane sulfones 2902
Propone sulfonic acid 2902
Propane sulfoxides 2902
Propane polysulfides 2902
Propionic acid 2638, 2682
—, hydration of, rate of 2909
—, manufacture cellulose acetate soluble in 2586
Propionic anhydride 2604, 2635, 2638
—, hydration, rate of 2909
—, manufacture 2908
Propionic ether, *see* Ethyl propionate.
Propionylamylaniline 2700
Propionylbutyaniline 2700
Propionylcellulose, *see* Cellulose propionate.
Propionyl chloride 2635
Propionylethylaniline 2700
Propionylhydrocellulose, *see* Hydrocellulose propionate.
Propionylmethylaniline 2700
Propionylpropylaniline 2700
Propyl acetate 2529, 2686
Propylacetanilid 2709
Propyl alcohol, miscibility of acetic acid with 2524
Propyl anthranilate 2692
iso-Propylbenzene 2549
Propyl benzoate 2692, 2693, 2697
—, cellulose acetate plastic with 2771
Propyl carbanilate 2715
Propyl chloride 2754
Propyl chlorstearate 2687, 2711
p-Propyl-*m*-cresol, *see* Thymol.
Propyl myristate 2687
Propyl palmitate 2687
Propyl phthalate 2715
Propyl silicate 2793
Propyl stearate 2687
Propyl succinate 2715
Propylene mercaptals 2902
Propane polysulfides 2902
Propylene sulfides 2902
Propylene sulfinic acid 2902
Propylene sulfones 2902
Propylene sulfonic acid 2902
Propylene sulfoxides 2902
Propylideneacetone, *see* Mesityl oxide.
Pseudocumol, *see* Cumene.
Pulegone 2679, 2715, 2760
Pulp, plastic of cellulose acetate and 2770
Pulp, wood, acetating 2568

Pumice stone, polishing linen with..... 2805
Pyrazolon derivatives 2715
Pyridine .2557, 2622, 2657, 2702, 2703, 2747, 2773, 2852, 2883
—, acetation in presence of.....2539, 2928
—, catalyst 2948
—, cellulose acetate lacquer containing..... 2853
—, cellulose benzoate solvent..... 2657
—, dextrin acetosulfates and..... 2949
—, dissolving ethyl cellulose by..... 2506
—, insolubility hydrated cellulose acetate in..... 2575
—, manufacture cellulose acetate soluble in.2546, 2561, 2586, 2776
—, manufacture cellulose formate soluble in..... 2626
—, solubility hydrated cellulose acetate in..... 2575
Pyridine acid sulfate.....2598, 2635
—, acetation with 2702
Pyridine sulfate, catalyst.....2940, 2948
Pyrocatechin, cellulose acetate solvent.....2666, 2671
—, plastic of cellulose acetate and..... 2766
Pyrocatechin diethyl ether 2671
—, plastic of cellulose acetate and..... 2766
Pyrocatechin monoethyl ether..... 2670
Pyrogallic acid, *see* Pyrogallol.
Pyragallol, cellulose acetate solvent..... 2666
—, developing with 2839
—, plastic of cellulose acetate and..... 2763
Pyrogallol di-salicylate 2692
Pyrogallol mono-acetate 2692
Pyrogallol triacetate 2662, 2685, 2692, 2693, 2795
Pyrophosphoric acid, *see* Phosphoric (pyro) acid.
Pyrosulfuryl chloride 2588, 2602, 2603, 2822
Pyroxylin, *see* Cellulose nitrate.

Quicklime, *see* Calcium oxide.
Quinic acid, acetyl derivatives of..... 2533
Quinoline 2702, 2703
—, acetation in presence of..... 2928
—, cellulose benzoate solvent..... 2657
—, dissolving ethyl cellulose by..... 2506
—, manufacture cellulose acetate soluble in..... 2546
Quinoline sulfate 2580, 2598, 2635
Quinols 2671
Quinone, acetation of..... 2538
—, action acetic anhydride on..... 2534

Radiators, lacquering, cellulose acetate for..... 2794
Radium rays, manufacture tetrachlorethane with..... 2742
Ramie, acetating 2568
Raw umber 2888
Rays, ultra violet, action of on cellulose acetate..... 2863
Real red E, dyeing cellulose acetate with..... 2840
Records, phonograph, *see* Phonograph records.
Refined fusel oil, *see* Fusel oil, refined.
Refractometer, analysis of acetic anhydride by..... 2914
Registers, lacquering, cellulose acetate for..... 2794

Resin, plastic of cellulose acetate and 2770
—, solvent, carbon tetrachloride as 2724
—, waterproofing wood with 2854
Resinates, metallic 2809
—, lacquers of cellulose acetate and 2956
Resin lacquer, cellulose acetate containing 2794, 2795
Resin lacquers 2798
Resins, aeroplane lacquer of cellulose acetate and 2883
—, cellulose acetate plastic of casein and 2772
—, combining cellulose acetate with 2882
—, dissolving, tetrachlorethane for 2749
—, estimation of 2924
—, plastic of cellulose acetate and 2710, 2764
—, synthetic formation of 2787, 2788
—, trichlorethylene solvent for 2731
Resorcin 2666, 2692, 2714, 2788, 2889
—, plastic of cellulose acetate and 2763
Resorcinol, *same as* Resorcin.
Resorcinol diacetate .. 2524, 2662, 2685, 2692, 2795, 2806, 2828, 2860, 2883, 2956
Resorcinol dimethyl ether 2666
Resorcinol monoacetate 2692
Resorcinol monomethyl ether 2666
Rhamnetin 2531
Rhinoceros, imitating hide of 2808
Rhodamine, dyeing cellulose acetate with 2836
Rhoduline heliotrope 2738, 2810
Ribbons, cellulose acetate 2763
Rice starch, *see* Starch, rice.
Ricinoleic acid 2681
Roentgen rays, fabrics impermeable to 2810
—, manufacture tetrachlorethane with 2742
Roofing paper, impregnating 2682
Rosanthrene, dyestuffs 2628
—, dyeing cellulose acetate with 2841
Rosanthrene A 2841, 2842
Rosemary oil 2704
Rosewood, imitating by lacquer 2799
Rosin 2956
—, plastic of cellulose acetate, naphthalene and 2710
Rubber, artificial, manufacture, cellulose acetate for 2835
—, carbon tetrachloride as solvent for 2725
—, cellulose acetate, plastic of casein, and 2772
—, coating wire with 2848
—, combining cellulose acetate with 2887
—, imitation, cellulose acetate for 2884, 2886
—, insulating wire with 2849
—, resins, cellulose acetate and 2772
—, solvent, perchlorethylene 2749
—, —, tetrachlorethane 2749
Rubber foam, manufacture, cellulose acetate for 2886, 2887
Rubber resin, combining cellulose acetate with 2772
Rubber resins 2731
Ruthenium red 2832

Saccharide acetate 2615
Saccharides 2501
—, acetated 2615
Saccharolactic acid, *see* Mucic acid.
Saccharose 2773
Saccharose acetate 2616, 2664, 2713
Saccharose heptacetate 2713, 2774
Saccharose monoacetate 2713, 2774
Saccharose octacetate 2713, 2774
Saccharose tetracetate 2713, 2774
Saffranin 2797, 2810, 2838
Safrol 2764, 2728, 2768, 2893
—, cellulose acetate solvent 2666
—, cellulose nitrate solvent 2666
iso-Safrol 2768
Salacetol 2679, 2715
Salantol 2679
Salicyl-acetol 2679
Salicyl-acetyl methyl alcohol 2679
Salicylic acid, ester, plastic of cellulose acetate and 2763
—, glyceryl esters of 2691
—, glycol ester of 2688
"Salicylic acid ester" 2773
Salicylic aldehyde 2538
Salicylous acid 2682
Saligenin 2668, 2669
—, plastic of cellulose acetate 2763
Saligallol 2693
Salinaphthol, *see* Betol.
Salol, *see* Phenyl salicylate.
Salves, cellulose acetate for 2889
Sandalwood oil 2704
Sandarac, *see also* Resins.
—, ... 2795, 2800
—, dichlorethylene solvent of 2726
—, solvents for 2791
—, tetrachlorethane solvent of 2744
—, wood oil solvent for 2719
Santal oil methyl ether 2688
Sawdust, acetic acid from 2521
Schoppers machine 2831
Schotten-Baumann reaction 2656
Sealing bottles, *see* Bottles, capping.
Seals, cellulose acetate for 2881
—, hydrated cellulose acetate for 2881
Sebacic ether, *see* Ethyl sebacate.
Sebacine 2774
Sebacinic ether, *see* Ethyl sebacate.
Selenious oxide, detecting acetic anhydride with 2909
Senegal gum 2823
Sensitiveness, emulsion, testing 2874
Sericose 2561, 2785, 2806
—, applications 2785, 2786
—, printing with 2785
—, properties 2788, 2789
Sericose L, *see* Sericose.

Sheet films, *see* Films, and Films, photographic.
Sheets, cellulose acetate 2860
—, —, hydrating 2584
—, —, manufacture of 2764
—, —, —, Lederer process 2860
—, —, —, Waite process 2860
—, —, —, Zuehl process 2860
—, —, partial hydrolysis of 2841
Shellac, *see also* Resins.
—, ... 2672, 2803
—, aeroplane lacquer of cellulose acetate and 2883
—, coating with cellulose acetate 2902
—, manufacture stereotypes with cellulose esters and 2855
—, plastic, cellulose acetate and 2698, 2766, 2770
—, —, aniline resinate and 2766
—, solvents for 2791
—, stiffening hats with 2815
—, tetrachlorethane solvent of 2744
—, wood oil solvent for 2719
Shields, wind 2871
Shirt fronts, waterproofing cellulose acetate for 2805, 2900
Shrinkage (of films), testing 2872
Sicoid 2783, 2784
Sienna 2888
Silicates, fireproofing with 2813
Silicic esters 2793
Silicic ethers 2688
Silicon compounds, aromatic 2768
Silicon tetrachloride 2521
Silk, artificial, *see* Filaments, artificial.
Silver, recovery of, from film 2792, 2807, 2875
—, —, —, by cyanide 2876
Silver acetate 2645
Silvered lace, manufacture of 2803, 2804
Silver nitrate 2804, 2858, 2859
Silver sulfide 2804
Silver yarns, cellulose acetate for 2825
Size (of films), determining 2872
Skins, *see* Hides.
Smaragdin 2890
Smokeless powder, *see also* Explosives.
—, cellulose acetate in 2846
—, cotton for manufacture of 2503
—, decomposition in, indicating, cellulose acetate for 2846
—, —, —, viscose for 2846
Smootching 2803
Soap, increasing porosity of cellulose acetate with 2838
—, solidifying alcohol by 2890
—, tetrachlorethane 2750
Sodium acetate 2521, 2532, 2565, 2592, 2787
—, acetation with 2535
—, anhydrous 2531
—, hydrolyzing cellulose acetate with 2958
—, manufacture 2614
—, —, acetic acid from 2903
—, —, acetic anhydride from 2526

Sodium acetate, neutralizing catalysts with 2579
—, precipitating cellulose acetate by 2573
Sodium acetylsulfate 2907
Sodium acid ethyl-sulfate 2594
Sodium bisulfate, purification of acetic acid with 2522
Sodium carbonate 2565, 2802
—, hydrating cellulose acetate with 2584
Sodium chlorate 2788
Sodium cresolate 2689
Sodium ethylate, preparation of 2923
Sodium ethyl sulfate 2593, 2955
Sodium formate, preparation of 2516
Sodium hydroxide, saponifying cellulose acetate by 2585
Sodium hypochlorite, decolorizing acetic acid with 2523
Sodium iodide 2677
Sodium margarate 2881
Sodium metantimonate 2793
Sodium metavanadate 2793
Sodium naphthionate, diazotization of 2840
Sodium naphtholate 2839
Sodium oleate 2881
Sodium palmitate 2881
Sodium paratungstate 2793
Sodium peroxide, bleaching cellulose acetate with 2612
Sodium phenolsulfonate 2590
Sodium phenylate 2689
Sodium propionate 2907
Sodium pyrosulfate, manufacture of formic acid with 2517
Sodium ricinosulfonate, *see* Sodium sulforicinate.
Sodium sebate 2891
Sodium selinite, detecting acetic anhydride with 2909
Sodium stearate 2881
Sodium sulforicinate 2587, 2810
Sodium sulforicinoleate 2587
Sodium sulfophenolate, *see* Sodium phenolsulfonate.
Sodium trichlorethylamidine 2714
Softeners, cellulose esters 2826
Solidified alcohol, *see* Alcohol, solidified.
Solid spirit 2890
Solubility determining 2918
—, modifying 2583
Soluble starch 2643
Solutions, bronze coating 2826
Solvace 2745
Solvent L 2673, 2674
Solvent naphtha 2756
Solvent recovery 2718
Solvents, *see also* Plastics.
—, ... 2659
—, casein 2773
—, cellulose acetate 2773
—, cellulose acetate and casein 2773
—, dehydrating 2718
—, miscibility of acetic acid with 2524
—, starch acetate 2934
Soudan dyestuffs, use of, in lacquering 2797

Soudan I, dyeing cellulose acetate with..... 2839
Soudan III, dyeing cellulose acetate with..... 2839
Sound record, *see* Phonograph record.
Sound undulations, recording cellulose acetate for..... 2880
Spanish leather, *see* Leather, Spanish.
Specimens, herbarium, preserving, Cellit for..... 2782
Spectroscopes, lacquering, cellulose acetate for..... 2797
Sprinkler tops, lacquering, cellulose acetate for..... 2798
Spinning rollers, cellulose acetate for, covering..... 2903
Spirit, solidified 2890
Spirosal, *see* Glycol monosalicylate.
Splints, celluloid 2890
—, cellulose acetate for, manufacture of..... 2890
—, surgical, *see* Surgical splints.
"Splits," coating with cellulose acetate..... 2814
Sponge, artificial, cellulose acetate for.....2834, 2956
—, —, cellulose nitrate for..... 2956
—, —, viscose for 2956
"Stability factor," determining..... 2920
Stability tests, cellulose acetate..... 2919
Stannous, *see* Tin(ous).
Stannic, *see* Tin (ic).
Star solvent 2686
Starch 2501, 2520
—, acetated, *see* Starch acetate.
—, acetylation 2927, 2951, 2952
—, —, catalyzers for 2932
—, —, superficial 2501, 2939
—, corn, acetating 2643
—, dissolving 2680
—, dyeing before acetation..... 2841
—, etherification of 2509
—, fermentation, acetone from..... 2674
—, formylation of 2520, 2641, 2648
—, methylation of 2509
—, molecular weight of..... 2928
—, plastic of cellulose acetate and..... 2785
—, potato, acetating 2643, 2645
—, rice, acetating 2643, 2645
—, —, treating yarn with..... 2823
—, soluble, *see also* Starch, acetylated.
—, —, ...2894, 2927
—, —, acetating 2645, 2646
—, —, acetochloro derivatives of..... 2645
—, —, benzoylating 2646, 2655
—, —, manufacture 2648, 2896
—, wheat, acetating 2645
Stays, steel, tipping ends of..... 2798
Starch acetate, 2501, 2642, 2646, 2648, 2932, 2933, 2934, 2935, 2951
—, decomposition of 2932
—, hydrolysis of 2927
—, iodine reaction with..... 2897
—, manufacture of 2525, 2893, 2894
—, —, Dixon process 2897
—, —, Pregl process 2645
—, —, Traquair process 2647

Starch acetate, microscopy of....2933, 2934
—, properties....2647, 2894, 2897, 2934, 2942
—, saponification of....2932, 2942
—, sizing paper with.... 2896
—, solvents of.... 2934
—, uses....2894, 2895
—, —, in confectionery.... 2895
—, water soluble....2934, 2935
Starch formate, manufacture.... 2641
—, properties.... 2642
Starch formylated, manufacture, Dixon process.... 2897
Starch hexacetate.... 2935
Starch triformate, *see* Starch formate.
Starched linen, *see* Linen, starched.
Steaoptens.... 2704
Steam pipe, lacquering, cellulose acetate for.... 2794
Stenciled work, lacquering, cellulose acetate for.... 2816
Stereotype paper, cellulose acetate for.... 2817
Stereotypes, cellulose esters for.... 2855
Stearic acid.... 2893
—, chlorinated....2676, 2681, 2880
Stearine, *see also* Tristearin.
—, dissolving ethyl cellulose by.... 2506
—, solidifying alcohol by.... 2891
Sthenosage.... 2834
Storage battery plates, cellulose butyrate for.... 2639
Storax....2708, 2888, 2893
Stripes, printing, cellulose acetate for.... 2786
Strontium caprylate.... 2888
Strontium chloride.... 2859
Styracin, *see* Cinnamyl cinnamate.
Styrax, *see* Storax.
Styrone.... 2704
Styryl alcohol, *see* Styrone.
Succinic acid, distribution of acetic acid and.... 2909
—, glycol ester of.... 2688
Succinic ether, *see* Ethyl succinate.
Sucrose octacetate.... 2644
Sugar, camphor substitute.... 2713
—, manufacture artificial sponge with cellulose acetate and.. 2835
Sulfacetic acid.... 2601
—, hydrolyzing cellulose acetate with.... 2578
o-Sulfamidoethyl ester.... 2714
Sulfamidoethyl ester.... 2714
Sulfides, combining cellulose acetate with.... 2902
Sulfinic acid, acetating cellulose with....2589, 2821
—, combining cellulose acetate with.... 2902
Sulfite cellulose, *see* Cellulose, sulfite.
Sulfoacetic acid....2595, 2958
—, hydrolyzing cellulose acetate with.... 2578
Sulfocyanides, cellulose acetate solvent.... 2665
—, solubility cellulose formates in.... 2619
Sulfones, combining cellulose acetate with.... 2902
Sulfonic acids.... 2590
—, acetating cellulose with.... 2589
—, acetation with.... 2538

Sulfonic acids, combining cellulose acetate with..... 2902
—, manufacture of formic acid with..... 2517
Sulfonic esters 2550
Sulfophenolic acid, *see* Phenol sulfonic acid.
Sulforicinic acid 2587
Sulforicinoleic acid 2587
Sulfoxides, combining cellulose acetate with..... 2902
Sulfur, combining cellulose acetate with..... 2901
—, recovery, tetrachlorethane for..... 2750
—, trichlorethylene solvent for..... 2731
—, waterproofing wood with..... 2854
Sulfurated tetraphenyl cellulose..... 2657
Sulfur chloride 2614, 2882, 2887
—, manufacture of 2526
—, manufacture acetic anhydride with..... 2526
Sulfur chlorides 2603
Sulfur dichloride 2722
Sulfur dioxide, *see* Sulfurous acid.
Sulfuric acid, acetation with..... 2538
—, acetation of, in acetylation..... 2535
—, anhydrochlorides 2602
—, catalytic action 2532
—, cleansing cellulose acetate articles with..... 2771
—, estimation of 2926
—, fuming, acetating with..... 2589
Sulfuric ether, *see* Ethyl ether; Diethyl ether.
Sulfurous acid 2521
—, bleaching paints with..... 2773
Sulfur trioxide, manufacture carbonyl chloride from..... 2588
Sulfuryl chloride 2602, 2603, 2614
—, formylation in presence of..... 2626
—, manufacture acetic anhydride from.....2527, 2909
Sulpholysis 2514, 2515
Sumatra camphor, *see* Borneol.
Surgery, acetated cellulose in..... 2534
Surgical jackets, celluloid for..... 2890
—, cellulose acetate for..... 2890
—, manufacture, cellulose acetate for..... 2900
Surgical splints, manufacture, cellulose acetate for..... 2900

Table cloths, damask effects on, cellulose acetate for..... 2786
—, waterproofing, cellulose acetate for..... 2805
Talc, polishing linen with..... 2805
Tallow, waterproofing wood with..... 2854
Tannin 2530, 2787, 2870, 2889
Tartaric acid 2682
—, glycol ester of..... 2688
—, hydrating cellulose esters with..... 2576
Tartaric acid esters, solubility of cellulose acetate in..... 2607
Tartaric ether, *see* Ethyl tartrate.
Telephone wire, insulating, cellulose acetate for..... 2852
Tensile strength, determining..... 2919
Terebene 2704, 2707
Terebentene, *see* Pinene.
Terpenes 2893

Terpenes, oxidation of 2522
—, precipitating cellulose acetate by..... 2820
Terpineol 2704
Terpin hydrate 2704
Terpinol 2704
Tetrabromethane, increasing solubility cellulose acetate by... 2955
Tetracetylcellulose 2534
Tetracetylchlorodextrose 2616, 2645
Tetracetylchlorogalactose 2616
Tetracetyldiglucose 2713
Tetracetylgalactose 2616
Tetracetyllactose 2713
Tetracetyl mannit, *see* Mannit tetracetate.
Tetracetylmethylglucoside 2616
Tetracetylmucic acid 2535
p-Tetrachloramidobenzene 2706
p-Tetrachlorbenzene *2706*
p-Tetrachlordiamidobenzene 2706
Tetrachlorethane 2661, 2739
1-1-2-2-Tetrachlorethane *2739*
Tetrachlorethane, cellulose benzoate solvent..... 2657
—, dissolving cellulose acetate and casein with..... 2773
—, dissolving ethyl cellulose by..... *2506*
—, manufacture 2739, 2740, 2741, 2742
—, —, Askenasy process 2740
—, —, Colson process *2740*
—, —, Griesheim process 2742
—, —, Lidholm process 2742
—, —, Michel process 2741
—, —, Mouneyrat process 2740
—, —, Sabanejeff process 2740
—, —, Tompkins process 2740
—, —, Voight process 2742
—, manufacture cellulose acetate soluble in.....2574, 2585
—, manufacture dichlorethylene from..... 2725
—, manufacture trichlorethylene from..... 2739
—, narcosis of 2749
—, plastic of cellulose acetate and.....2762, 2764
—, properties 2743, 2744
—, solubility, cellulose propionate in..... 2638
—, solubility of 2744
—, solvent of alcohol and..... 2746
—, substitute for 2768
—, testing 2750, 2751
—, toxicity 2730
—, uninflammable lacquers with..... 2720
—, use in cellulose acetate lacquers.....2747, 2795, 2796
—, uses 2748, 2750
Tetrachlorethylacetanilid 2701, 2703, 2767
Tetrachlorethylene, *see* Perchlorethylene.
Tetrachlorinated ethane, *see* Tetrachlorethane.
Tetrachlormethane, *see* Carbon tetrachloride.
Tetrachlornaphthalene 2747
Tetrachlornaphthol 2682
Tetrachlornaphthol phosphate 2682
Tetrachlorphenol 2682

Tetrachlorphenol phosphate 2682
Tetramethyl-glucose 2898
Tetranitrodinaphthyl phosphate 2682
Tetranitromethane 2703
Tetraphenyl cellulose 2657
Tetraphenyl cellulose sulfonate..... 2657
Tetraphenyl urea 2698, 2716
Textile finishes, *see* Finishes, textile.
Textiles, *see also* Fabrics.
—, acetation, superficial 2555
—, damask effect on, producing..... 2561
—, —, cellulose acetate for..... 2788
—, finishing, acetated starch for..... 2895
—, mat effects on..... 2788
—, moire effects on, cellulose acetate for producing..... 2788
—, printing on, cellulose acetate for..... 2806
—, waterproof, Goldstein method..... 2813
—, waterproof impressions, cellulose acetate for..... 2824
—, waterproofing 2555
—, —, cellulose acetate for.....2806, 2901
Thanatol 2670
Thermoplastic, *see* Plastic.
Thermoplastic cellulose acetate, *see* Cellulose acetate, thermoplastic.
Thickeners for textiles 2785
Thickness (of films), testing..... 2872
Thiocyanates, *see* Sulfocyanides.
Thioglycerol 2902
Thioglycerol mercaptans 2902
Thioglycerol polysulfides 2902
Thioglycerol sulfides 2902
Thioglycerol mercaptals 2902
Thioglyceryl sulfinic acid..... 2902
Thioglyceryl sulfones 2902
Thioglyceryl sulfonic acid..... 2902
Thioglyceryl sulfoxides 2902
Thiopyroglycides 2902
Thorium nitrate 2729
Thorium oxide 2729
Thread, *see also* Filaments, artificial.
Thread, filling with cellulose acetate..... 2823
—, imparting brilliance to, cellulose acetate for..... 2823
—, increasing pliability of, cellulose acetate for..... 2823
—, increasing softness of, cellulose acetate for..... 2823
—, cellulose acetate 2763
—, coated, softening 2826
—, coating with metals, cellulose acetate for..... 2825
Thuja oil 2715
Thujone 2715
Thymene 2704
Thymic acid, *see* Thymol.
Thymol 2668, 2669, 2715, 2761
—, plastic of cellulose acetate and..... 2700
Thyresol 2688
Tin (ic) chloride, cellulose acetate solvent..... 2665
—, dissolving cellulose acetate by..... 2800
Tin (ous) chloride....2597, 2711, 2951, 2952, 2953, 2954, 2957

Tin (ous), acetation with 2538
—, catalyzer 2939, 2940
—, reducing inflammability of, cellulose acetate for 2610
Tin tetrachloride, *see* Tin (ic) chloride.
Tire covers, canvas, rot-proofing with cellulose acetate 2900
Tissue paper, acetating 2505, 2554, 2568
Tobacco, aroma, preserving with cellulose acetate 2887
Tobacco, discoloration from, preventing by cellulose acetate .. 2887
Tolodine 2711
Tolu balsam 2692, 2708, 2888, 2893
Toluene 2758, 2885
—, acetation in presence of 2565
—, cellulose acetate solvent of alcohol, and 2664
—, dissolving ethyl cellulose by 2506
—, inhibiting acetation with 2606
—, insolubility hydrated cellulose acetate in 2575
—, manufacture cellulose acetate soluble in alcohol and 2582
—, precipitating cellulose acetate by 2820
—, solubility cellulose propionate in 2638
p-Toluenesulfoacidphenylether 2714
p-Toluene sulfamid 2703, 2714, 2775
p-Toluenesulfamido acetic acid 2714
p-Toluenesulfamido ethyl ester 2714
p-Toluenesulfoanilid 2714
Toluenesulfocellulose, *see* Cellulose toluenesulfonate.
p-Toluenesulfo-*p*-chloranilid 2714
p-Toluenesulfocresol 2714
p-Toluenesulfodiethylamid 2714
p-Toluenesulfodiphenylamine 2714
p-Toluenesulfoethylamid 2714
p-Toluenesulfoethylanilid 2714
p-Toluenesulfomethylanilid 2714
p-Toluenesulfomonoethylamid 2714
p-Toluenesulfo-*a*-naphthol 2714
p-Toluenesulfo-*b*-naphthol 2714
p-Toluenesulfo-*a*-naphthylamin 2714
p-Toluenesulfo-*b*-naphthylamin 2714
p-Toluenesulfo-*o*-phenetidin 2714
p-Toluenesulfo-*p*-phenetidin 2714
p-Toluenesulfophenylhydrazin 2714
p-Toluenesulfo-*o*-toluid 2714
p-Toluenesulfo-*m*-xylidid 2714
Toluenesulfonic esters 2697
Toluic acid, glycol ester of 2688
Toluidine 2698
—, cellulose benzoate solvent 2657
—, dissolving ethyl cellulose by 2506
—, hydrolyzing cellulose acetate with 2578
o-Toluidine 2810
o-Toluidine bisulfate 2595
o-Toluidine sulfate 2595
p-Toluidine sulfamide, manufacture, plastic cellulose acetate films with 2765
Toluidines, alkylated, acetylating 2701
Toluol, *see* Toluene.
Toluol chlorides 2715

Toluol-sulfamid 2767
p-Toluolsulfochloride 2654
Toluol-sulfonamid 2704
p-Toluyl chloride 2544
m-Toluylenediamine, *see* 1, 3, 5-Toluylenediamine.
1, 3, 5-Toluylenediamine, diazotization of..... 2839
Toluylenediamines 2706
o-Toluylenemethenylamid 2706
Tolyl 2714
o-Tolylacetamide, *see* *o*-Acettoluide.
Tolyl acetate 2692
Toys, lacquering, cellulose acetate for..... 2798
Tracing cloth, manufacture, cellulose acetate for..... 2902
Tragacanth 2785
—, substitute for, acetated starch as..... 2896
Transparent paper, *see* Paper, transparent.
Travelers' alcohol 2890
"Tri" 2734
Triacetate of dulcite, *see* Dulcite triacetate.
Triacetic cellulose, *see* Cellulose acetate.
Triacetin, *see* Glyceryl triacetate.
Triacetyldiglucose 2718
Triacetyloxycellulose 2536
Tribromphenol 2668
s-Tribromphenol 2539
—, acetation of 2538
Trichloracetic acid.....2543, 2600, 2933, 2951, 2952, 2953, 2954
—, catalyzer 2932, 2933, 2936, 2942
—, removing corns by cellulose acetate and..... 2889
Trichloraldehyde, *see* Chloral.
Trichloraniline 2699, 2716, 2781
as-Trichlorbenzene 2706
as-Trichlordiamidobenzene 2706
Trichlorethane 2661, 2804
Trichlorethylamidine 2714
Trichlorethylene.....2667, 2728, 2733, 2740, 2762, 2772, 2795
2800, 2804, 2900, 2956
—, action on metals..... 2731
—, combining cellulose acetate, phenol and..... 2903
—, decomposition of.....2732, 2733
—, degreasing cotton with..... 2503
—, density 2730
—, derivatives of 2729
—, furniture polish containing..... 2747
—, manufacture 2728, 2729, 2730, 2741
—, —, Berthelot process 2728
—, —, Fischer process 2728
—, miscibility with solvents..... 2730
—, narcosis of..... 2732
—, physiological action 2732
—, properties 2730
—, saponification of 2733
—, solvent 2731
—, toxicity 2730
—, uninflammable lacquers with..... 2720
Trichlorhydrin 2704, 2739

Trichlormethane, *see* Chloroform.
Trichlormethylacetanilid 2701, 2703, 2767
Trichloromercuriacetaldehyde 2527
Trichlorphenol 2668, 2684
—, cellulose acetate solvent 2666
Trichlorpropyl acetanilid 2703
Tricresyl borate 2768
Tricresyldinitrotrinaphthyl thiophosphate 2682, 2683
Tricresyl phosphate ...2584, 2682, 2690, 2701, 2703, 2767, 2795
—, dissolving ethyl cellulose by 2506
o-Tricresyl phosphate 2809, 2810
Tricresyl thiophosphate 2682
Triformin, *see* Glyceryl formate.
Triglucose acetate 2532
Trihydric carbocyclic alcoholic esters 2692
unsym-Trimethylbenzene, *see* Cumene.
Trimethylethylene 2698
Trimethyl-glucose 2898
Trimethyl-glucose osazone 2898
Trimmings, cellulose acetate for 2829
Trinaphthyl phosphate 2682
Tri-*α*-naphthyl phosphate 2683
Tri-*b*-naphthyl phosphate 2683
Trinaphthyl phosphate, celluloid substitute containing 2581
Trinaphthyl thiophosphate 2682
Trinitrophenetol 2768
Trinitrotoluene 2902
Trioxyacetophenon 2709
Trioxybenzophenon 2709
Triphenylamine 2699
Triphenyl borate 2685, 2768, 2826
Triphenyl phosphate...2583, 2608, 2629, 2632, 2682, 2684, 2690, 2701, 2703, 2705, 2767, 2795, 2826
—, cellulose-substitute containing 2581
—, cellulose acetate and 2761
—, dissolving cellulose phospho-formate by 2632
—, dissolving ethyl cellulose by 2506
Triphenyl thiophosphate 2682
Tripropionylcellulose 2638
Tristearin (*see also* Stearin) 2891
Tri-thiopyroglycide 2902
Tri-*o*-tolyl phosphate 2683
Tri-*p*-tolyl phosphate 2683
Tuberculosis, trichlorethylene for 2733
Tubes, cellulose acetate 2763
—, coating with cellulose acetate 2807
—, lacquering, cellulose acetate for 2798
Tulle, coating 2811
—, manufacture of 2827
—, —, cellulose acetate for 2827
Tung oil 2809, 2810
—, dissolving ethyl cellulose by 2506
Tungstates 2793
—, fireproofing with 2813
Turkey red oil, *see* Sodium sulforicinate.
Turpentine 2704

Turpentine, acetated 2697
—, chlorinating 2707
—, detecting water in acetic acid with..... 2907
—, oxidation to acetic acid..... 2519
—, plastic of cellulose acetate and..... 2766
—, precipitating cellulose acetate by..... 2820
—, spirits of, determining strength of acetic acid with..... 2524
—, Venice, *see* Venice turpentine.
Turpentine oil, *see* Oil of turpentine.
Tussah silk 2827

Ultra violet rays. *see* Rays. ultra violet.
—, manufacture tetrachlorethane by 2742
Umber, burnt 2888
—, raw 2888
Urea 2629, 2683, 2697, 2852
—, stabilizer for cellulose acetate..... 2608
Urea acetate 2697
Ureas 2698
—, tetrasubstituted 2708
Urethanes 2715

Valerianic acid 2682
Valerianic ether, *see* Ethyl valerianate.
Valeric acid, *see* Valerianic acid.
Valerone, *see* Di-isobutyl ketone.
Valerylamylaniline 2700
Valerylbutylaniline 2700
Valerylethylaniline 2700
Valerylhydrocellulose, *see* Hydrocellulose valerianate.
Valerylmethylaniline 2700
Valerylpropylaniline 2700
Vanadates 2793
Vanadium, manufacture acetic acid with aldehyde and compounds of 2522
Vanadium oxide 2521
Vanadium pentoxide 2521
Vanillic acid, glycol ester of..... 2688
Varnish, anti-fouling 2772
—, infusible, insulating 2852
—, linseed oil 2883
—, poppyseed oil 2883
Varnishes, *see also* Lacquers, Paints.
—, cellulose acetate for.....2731, 2903
Varnish solvent, carbon tetrachloride for..... 2725
Vaseline, *see also* Paraffin, Mineral oils, etc.
—, dissolving ethyl cellulose by..... 2506
—, plastic of cellulose acetate and..... 2766
Vehicle, pharmaceutical, cellulose acetate as.....2889, 2890
Veilings, manufacture of, cellulose acetate for..... 2827
Venice turpentine.....2633, 2848, 2852, 2888, 2889
—, coating wire with.....2847, 2848, 2849
Veratrol, *see* Catechol dimethyl ether.
Veratrol 2768

Veratrol, cellulose acetate solvent 2666
Veronal 2697
Vessels, bottom of, paints for 2773
Vetiver 2893
Victoria green 2797, 2810, 2852
Vinyl alcohol, esters of 2685
—, —, manufacture 2932
Vinyl ethers, manufacture 2932
Viscoid 2536
Viscose, *see also* Cellulose xanthate.
—, ... 2505, 2536, 2809, 2888
—, acetation of 2562, 2928
—, action ultra violet rays on 2864
—, artificial sponge for 2956
—, benzoylation of 2654
—, coating with cellulose acetate 2813
—, combining cellulose acetate with 2901
—, ethyl cellulose from 2507
—, films of, coating with cellulose acetate 2863
—, formylating 2620, 2628
—, impregnating wood with 2854
—, indicating decomposition in smokeless powder by 2846
—, manufacture artificial filaments of 2957
—, manufacture artificial sponge from 2834, 2835
—, plastic 2773
—, plastic of albumin and 2773
—, plastic of casein and 2773
—, waterproofing with cellulose acetate 2855
—, waterproofing with cellulose nitrate 2855
Viscosimeter, Cochius 2918
—, Henry 2918
—, Redwood 2918
Viscosity, determining 2918
Vitran 2739
Vitrol 2739

Wall-papers, cellulose acetate for 2829
Warts, removal of, cellulose acetate for 2889
Waste film, *see* Film, waste.
Water, action of, on cotton 2503
—, binary solution equilibrium between acetic acid and 2525
—, determination of in cellulose 2502
—, hydrating cellulose esters with 2576
—, ozonized 2731
Waterproofing, cellulose acetate for 2899
—, cellulose butyrate for 2639
Watt-meters, bushings of, manufacture, cellulose acetate for .. 2851
Watt-meter shafts, bushings for, cellulose acetate in manufacture of 2851
Wax, plastic of cellulose acetate and 2766
—, solidifying alcohol by 2891
—, solvent, carbon tetrachloride for 2724
Waxed cloth, *see* Cloth, waxed.
—, cellulose acetate for 2810
Waxed paper, cellulose acetate for 2810

Welsbach mantles, *see* Mantles, incandescent.
Westron 2739
Westrosol 2733
White birch, *see* Birch.
White enamels 2798
—, cellulose acetate, formula for..... 2798
—, properties of..... 2798
Window panes, cellulose acetate..... 2879
Wind shields, cellulose acetate.....2871, 2879
Wings, biplane, impregnating, cellulose acetate for.2883, 2884, 2885
—, monoplane, impregnating, cellulose acetate for.2883, 2884, 2885
Wintergreen oil, *see also* Methyl salicylate.
Wire, cellulose acetate coated, dyeing..... 2852
—, —, —, properties of 2854
—, coating, cellulose acetate for..... 2826
—, insulated, detecting defective spots in..... 2848
—, insulation, Cellit for..... 2778
—, —, cellulose acetate for, 2747, 2847, 2848, 2849, 2850, 2851, 2853, 2854
—, —, cellulose acetate and hexachlorethane for..... 2755
—, —, cellulose benzoate for.....2641, 2658
—, —, cellulose butyrate for..... 2639
—, —, cellulose formate for..... 2633
—, —, cellulose nitrate for..... 2851
—, —, collodion for 2851
Wood, *see also* Cellulose, Cotton, Paper.
—, artificial, cellulose esters in the manufacture of..... 2855
—, birch, acetating 2568
—, distillation, solvents from..... 2719
—, imitating by lacquer..... 2799
—, impregnating, cellulose acetate for..... 2854
—, —, viscose for 2854
—, lacquering, cellulose acetate for.....2784, 2792
—, manufacture oxycellulose from..... 2537
—, —, cellulose acetate for..... 2854
—, preservation, acetone oil for..... 2678
—, —, tetrachlorethane for 2747
—, —, trichlorethylene for 2747
Wood cellulose, *see* Cellulose, wood.
Wood meal, coating fabrics with cellulose acetate and..... 2900
Wood oil, *see also* Tung oil..... 2719
Wood pulp, *see* Cellulose, wood.
—, acetating 2568
—, impregnating with cellulose acetate..... 2855
Wool, acetone from 2677
—, degreasing, tetrachlorethane for..... 2750
Wool washings, acetone from..... 2678
Wounds, use of cellulose acetate in..... 2889
Wrought black lacquers..... 2799

Xanthates, dissolving cellulose formate with..... 2632
Xylene 2706, 2758
—, dissolving ethyl cellulose by..... 2506
—, distilling acetic acid in presence of..... 2520
—, inhibiting acetation with..... 2606

Xylene, insolubility hydrated cellulose acetate in 2575
—, precipitation of cellulose acetate by 2793, 2820
—, solubility cellulose propionate in 2638
Xylenes 2756
Xylidine 2698
—, cellulose benzoate solvent 2657
—, hydrolyzing cellulose acetate with 2578
Xylol, *see* Xylene.
Xylyl acetate 2692
Xylyl compounds 2714

Yarn, acetation, superficial 2555
Yarns, coating, mechanical appliance for 2826
—, coating with cellulose esters 2823
—, dichroic, *see* Yarn, fluorescent.
—, fluorescent, producing 2827
—, metallized, cellulose acetate for 2825, 2827
Yield, cellulose triacetate 2575

Zellit 2774
Zellith 2774
Zinc, electrolytic recovery of 2725
—, salts of, anti-fouling paint containing 2731
Zinc acetate 2536, 2556, 2557
—, acetating with 2534, 2928
Zinc carbonate, enamels containing 2798
Zinc chloride 2597
—, acetation with 2533, 2538, 2575, 2928
—, catalyst 2532, 2957
—, dissolving cellulose by 2533
—, dissolving cellulose acetate by 2800
—, dissolving cellulose formate in 2623
—, hydrating with 2580
—, manufacture cellulose butyrate with 2639
—, overcoming brittleness in cellulose acetate films with 2769
Zinc oleate 2809
Zinc oxide, enamel containing 2798
—, printing with 2786
Zinc palmitate 2809
Zinc propionate 2635
Zinc ricinoleate 2711
Zinc stearate 2809
Zinc sulfate 2597, 2798
—, acetation with 2538
Zinc sulfide 2801, 2805
—, white enamels containing 2798
Zinc viscose 2809
Zymene 2745

MAR 2 1 1916

D. VAN NOSTRAND COMPANY

25 PARK PLACE

NEW YORK

SHORT-TITLE CATALOG

OF

Publications and Importations

OF

SCIENTIFIC AND ENGINEERING BOOKS

This list includes all the books published by the
M. C. CLARK PUBLISHING CO.,
Chicago, Ill.,
and the technical publications of the following English publishers:
SCOTT, GREENWOOD & CO. JAMES MUNRO & CO., Ltd.
CONSTABLE & COMPANY, Ltd. TECHNICAL PUBLISHING CO.
ELECTRICIAN PRINTING & PUBLISHING CO.
for whom D. Van Nostrand Company are American agents.

SHORT-TITLE CATALOG

OF THE

Publications and Importations

OF

D. VAN NOSTRAND COMPANY

25 PARK PLACE, N. Y.

The books published by the
MYRON C. CLARK PUBLISHING CO., Chicago, Ill.
are included in this catalog.

Prices marked with an asterisk (*) are NET.
All bindings are in cloth unless otherwise noted.

Abbott, A. V.	The Electrical Transmission of Energy	8vo, *$5 00
——	A Treatise on Fuel. (Science Series No. 9.)	16mo, 0 50
——	Testing Machines. (Science Series No. 74.)	16mo, 0 50
Adam, P.	Practical Bookbinding. Trans. by T. E. Maw	12mo, *2 50
Adams, H.	Theory and Practice in Designing	8vo, *2 50
Adams, H. C.	Sewage of Sea Coast Towns	8vo *2 00
Adams, J. W.	Sewers and Drains for Populous Districts	8vo, 2 50
Addyman, F. T.	Practical X-Ray Work	8vo, *4 00
Adler, A. A.	Theory of Engineering Drawing	8vo, *2 00
——	Principles of Parallel Projecting-line Drawing	8vo, *1 00
Aikman, C. M.	Manures and the Principles of Manuring	8vo, 2 50
Aitken, W.	Manual of the Telephone	8vo, *8 00
d'Albe, E. E. F.,	Contemporary Chemistry	12mo, *1 25
Alexander, J. H.	Elementary Electrical Engineering	12mo, 2 00
Allan, W.	Strength of Beams Under Transverse Loads. (Science Series No. 19.)	16mo, 0 50
——	Theory of Arches. (Science Series No. 11.)	16mo,
Allen, H.	Modern Power Gas Producer Practice and Applications	12mo, *2 50
——	Gas and Oil Engines	8vo, *4 50
Anderson, F. A.	Boiler Feed Water	8vo, *2 50
Anderson, Capt. G. L.	Handbook for the Use of Electricians	8vo, 3 00
Anderson, J. W.	Prospector's Handbook	12mo, 1 50
Andés, L.	Vegetable Fats and Oils	8vo, *4 00
——	Animal Fats and Oils. Trans. by C. Salter	8vo, *4 00
——	Drying Oils, Boiled Oil, and Solid and Liquid Driers	8vo, *5 00
——	Iron Corrosion, Anti-fouling and Anti-corrosive Paints. Trans. by C. Salter	8vo, *4 00
Andés, L.	Oil Colors, and Printers' Ink. Trans. by A. Morris and H. Robson	8vo, *2 50

Andés, L. Treatment of Paper for Special Purposes. Trans. by C. Salter. 12mo, *2 50

Andrews, E. S. Reinforced Concrete Construction.....12mo, *1 25
—— Theory and Design of Structures.....8vo, *3 50
—— Further Problems in the Theory and Design of Structures....8vo, *2 50

Andrews, E. S., and Heywood, H. B. The Calculus for Engineers. 12mo, *1 25

Annual Reports on the Progress of Chemistry. Twelve Volumes now ready. Vol. I., 1904, Vol. XII., 1914.....8vo, each, *2 00

Argand, M. Imaginary Quantities. Translated from the French by A. S. Hardy. (Science Series No. 52.).....16mo, 0 50

Armstrong, R., and Idell, F. E. Chimneys for Furnaces and Steam Boilers. (Science Series No. 1.).....16mo, 0 50

Arnold, E. Armature Windings of Direct-Current Dynamos. Trans. by F. B. DeGress.....8vo, *2 00

Asch, W., and Asch, D. The Silicates in Chemistry and Commerce. 8vo, *6 00

Ashe, S. W., and Keiley, J. D. Electric Railways. Theoretically and Practically Treated. Vol. I. Rolling Stock.....12mo, *2 50

Ashe, S. W. Electric Railways. Vol. II. Engineering Preliminaries and Direct Current Sub-Stations.....12mo, *2 50
—— Electricity: Experimentally and Practically Applied.....12mo, *2 00

Ashley, R. H. Chemical Calculations.....12mo, *2 00

Atkins, W. Common Battery Telephony Simplified.....12mo, *1 25

Atkinson, A. A. Electrical and Magnetic Calculations.....8vo, *1 50

Atkinson, J. J. Friction of Air in Mines. (Science Series No. 14.)..16mo, 0 50

Atkinson, J. J., and Williams, Jr., E. H. Gases Met with in Coal Mines. (Science Series No. 13.).....16mo, 0 55

Atkinson, P. The Elements of Electric Lighting.....12mo, 1 00
—— The Elements of Dynamic Electricity and Magnetism.....12mo, 2 00
—— Power Transmitted by Electricity.....12mo, 2 00

Auchincloss, W. S. Link and Valve Motions Simplified.....8vo, *1 50

Austin, E. Single Phase Electric Railways.....4to, *5 00

Ayrton, H. The Electric Arc.....8vo, *5 00

Bacon, F. W. Treatise on the Richards Steam-Engine Indicator..12mo, 1 00

Bailes, G. M. Modern Mining Practice. Five Volumes.....8vo, each, 3 50

Bailey, R. D. The Brewers' Analyst.....8vo, *5 00

Baker, A. L. Quaternions.....8vo, *1 25
—— Thick-Lens Optics.....12mo, *1 50

Baker, Benj. Pressure of Earthwork. (Science Series No. 56.)...16mo,

Baker, I. O. Levelling. (Science Series No. 91.).....16mo, 0 50

Baker, M. N. Potable Water. (Science Series No. 61.).....16mo, 0 50
—— Sewerage and Sewage Purification. (Science Series No. 18.)..16mo, 0 50

Baker, T. T. Telegraphic Transmission of Photographs.....12mo, *1 25

Bale, G. R. Modern Iron Foundry Practice. Two Volumes. 12mo.
Vol. I. Foundry Equipment, Materials Used..... *2 50
Vol. II. Machine Moulding and Moulding Machines..... *1 50

Ball, J. W. Concrete Structures in Railways.....8vo, *2 50

Ball, R. S. Popular Guide to the Heavens.....8vo, *4 50

—— Natural Sources of Power. (Westminster Series.).....8vo, *2 00

Ball, W. V. Law Affecting Engineers.....8vo, *3 50

Bankson, Lloyd. Slide Valve Diagrams. (Science Series No. 108.) 16mo, 0 50
Barba, J. Use of Steel for Constructive Purposes 12mo, 1 00
Barham, G. B. Development of the Incandescent Electric Lamp 8vo, *2 00
Barker, A. F. Textiles and Their Manufacture. (Westminster Series.) 8vo, 2 00
Barker, A. F., and Midgley, E. Analysis of Textile Fabrics 8vo, 3 00
Barker, A. H. Graphic Methods of Engine Design 12mo, *1 50
—— Heating and Ventilation 4to, *8 00
Barnard, J. H. The Naval Militiaman's Guide 16mo, leather 1 00
Barnard, Major J. G. Rotary Motion. (Science Series No. 90.) 16mo, 0 50
Barrus, G. H. Boiler Tests 8vo, *3 00
—— Engine Tests 8vo, *4 00
The above two purchased together *6 00
Barwise, S. The Purification of Sewage 12mo, 3 50
Baterden, J. R. Timber. (Westminster Series.) 8vo, *2 00
Bates, E. L., and Charlesworth, F. Practical Mathematics 12mo,
Part I. Preliminary and Elementary Course *1 50
Part II. Advanced Course *1 50
—— Practical Mathematics 12mo, *1 50
—— Practical Geometry and Graphics 12mo, *2 00
Batey, J. The Science of Works Management 12mo, *1 25
Beadle, C. Chapters on Papermaking. Five Volumes 12mo, each, *2 00
Beaumont, R. Color in Woven Design 8vo, *6 00
—— Finishing of Textile Fabrics 8vo, *4 00
Beaumont, W. W. The Steam-Engine Indicator 8vo, 2 50
Bechhold, H. Colloids in Biology and Medicine. Trans. by J. G. Bullowa (*In Press.*)
Beckwith, A. Pottery 8vo, paper, 0 60
Bedell, F., and Pierce, C. A. Direct and Alternating Current Manual. 8vo, *2 00
Beech, F. Dyeing of Cotton Fabrics 8vo, *3 00
—— Dyeing of Woolen Fabrics 8vo, *3 50
Begtrup, J. The Slide Valve 8vo, *2 00
Beggs, G. E. Stresses in Railway Girders and Bridges (*In Press.*)
Bender, C. E. Continuous Bridges. (Science Series No. 26.) 16mo, 0 50
—— Proportions of Pins used in Bridges. (Science Series No. 4.) 16mo, 0 50
Bengough, G. D. Brass. (Metallurgy Series.) (*In Press.*)
Bennett, H. G. The Manufacture of Leather 8vo, *4 50
Bernthsen, A. A Text-book of Organic Chemistry. Trans. by G. M'Gowan 12mo, *2 50
Berry, W. J. Differential Equations of the First Species. 12mo. (*In Preparation.*)
Bersch, J. Manufacture of Mineral and Lake Pigments. Trans. by A. C. Wright 8vo, *5 00
Bertin, L. E. Marine Boilers. Trans. by L. S. Robertson 8vo, 5 00
Beveridge, J. Papermaker's Pocket Book 12mo, *4 00
Binnie, Sir A. Rainfall Reservoirs and Water Supply 8vo, *3 00
Binns, C. F. Manual of Practical Potting 8vo, *7 50
—— The Potter's Craft 12mo, *2 00
Birchmore, W. H. Interpretation of Gas Analysis 12mo, *1 25
Blaine, R. G. The Calculus and Its Applications 12mo, *1 50

Blake, W. H. Brewers' Vade Mecum 8vo, *4 00
Blasdale, W. C. Quantitative Chemical Analysis. (Van Nostrand's Textbooks.) 12mo, *2 50
Bligh, W. G. The Practical Design of Irrigation Works 8vo, *6 00
Bloch, L. Science of Illumination. Trans. by W. C. Clinton 8vo, *2 50
Blok, A. Illumination and Artificial Lighting 12mo, 1 25
Blücher, H. Modern Industrial Chemistry. Trans. by J. P. Millington. 8vo, *7 50
Blyth, A. W. Foods: Their Composition and Analysis 8vo, 7 50
—— Poisons: Their Effects and Detection 8vo, 7 50
Böckmann, F. Celluloid 12mo, *2 50
Bodmer, G. R. Hydraulic Motors and Turbines 12mo, 5 00
Boileau, J. T. Traverse Tables 8vo, 5 00
Bonney, G. E. The Electro-platers' Handbook 12mo, 1 20
Booth, N. Guide to the Ring-spinning Frame 12mo, *1 25
Booth, W. H. Water Softening and Treatment 8vo, *2 50
—— Superheaters and Superheating and Their Control 8vo, *1 50
Bottcher, A. Cranes: Their Construction, Mechanical Equipment and Working. Trans. by A. Tolhausen 4to, *10 00
Bottler, M. Modern Bleaching Agents. Trans. by C. Salter 12mo, *2 50
Bottone, S. R. Magnetos for Automobilists 12mo, *1 00
Boulton, S. B. Preservation of Timber. (Science Series No. 82.) 16mo, 0 50
Bourcart, E. Insecticides, Fungicides and Weedkillers 8vo, *4 50
Bourgougnon, A. Physical Problems. (Science Series No. 113.) 16mo, 0 50
Bourry, E. Treatise on Ceramic Industries. Trans. by A. B. Searle. 8vo, *5 00
Bowie, A. J., Jr. A Practical Treatise on Hydraulic Mining 8vo, 5 00
Bowles, O. Tables of Common Rocks. (Science Series No. 125.) 16mo, 0 50
Bowser, E. A. Elementary Treatise on Analytic Geometry 12mo, 1 75
—— Elementary Treatise on the Differential and Integral Calculus 12mo, 2 25
—— Elementary Treatise on Analytic Mechanics 12mo, 3 00
—— Elementary Treatise on Hydro-mechanics 12mo, 2 50
—— A Treatise on Roofs and Bridges 12mo, *2 25
Boycott, G. W. M. Compressed Air Work and Diving 8vo, *4.00
Bragg, E. M. Marine Engine Design 12mo, *2 00
—— Design of Marine Engines and Auxiliaries ..... (*In Press.*)
Brainard, F. R. The Sextant. (Science Series No. 101.) 16mo,
Brassey's Naval Annual for 1915 ..... 8vo,
Brew, W. Three-Phase Transmission 8vo, *2 00
Briggs, R., and Wolff, A. R. Steam-Heating. (Science Series No. 67.) 16mo, 0 50
Bright, C. The Life Story of Sir Charles Tilson Bright 8vo, *4 50
Brislee, T. J. Introduction to the Study of Fuel. (Outlines of Industrial Chemistry.) 8vo, *3 00
Broadfoot, S. K. Motors, Secondary Batteries. (Installation Manuals Series.) 12mo, *0 75
Broughton, H. H. Electric Cranes and Hoists *9 00
Brown, G. Healthy Foundations. (Science Series No. 80.) 16mo, 0 50
Brown, H. Irrigation 8vo, *5 00
Brown, Wm. N. The Art of Enamelling on Metal 12mo, *1 00

Brown, Wm. N. Dipping, Burnishing, Lacquering and Bronzing Brass Ware.....12mo, *1 00
—— Handbook on Japanning and Enamelling.....12mo, *1 50
—— House Decorating and Painting.....12mo, *1 50
—— History of Decorative Art.....12mo, *1 25
—— Workshop Wrinkles.....8vo, *1 00
Browne, C. L. Fitting and Erecting of Engines.....8vo, *1 50
Browne, R. E. Water Meters. (Science Series No. 81.).....16mo, 0 50
Bruce, E. M. Pure Food Tests.....12mo, *1 25
Bruhns, Dr. New Manual of Logarithms.....8vo, cloth, 2 00
half morocco, 2 50
Brunner, R. Manufacture of Lubricants, Shoe Polishes and Leather Dressings. Trans. by C. Salter.....8vo, *3 00
Buel, R. H. Safety Valves. (Science Series No. 21.).....16mo, 0 50
Burley, G. W. Lathes, Their Construction and Operation.....12mo, 1 25
Burstall, F. W. Energy Diagram for Gas. With Text.....8vo, 1 50
—— Diagram. Sold separately..... *1 00
Burt, W. A. Key to the Solar Compass.....16mo, leather, 2 50
Buskett, E. W. Fire Assaying.....12mo, *1 25
Butler, H. J. Motor Bodies and Chassis.....8vo, *2 50
Byers, H. G., and Knight, H. G. Notes on Qualitative Analysis....8vo, *1 50

Cain, W. Brief Course in the Calculus.....12mo, *1 75
—— Elastic Arches. (Science Series No. 48.).....16mo, 0 50
—— Maximum Stresses. (Science Series No. 38.).....16mo, 0 50
—— Practical Designing Retaining of Walls. (Science Series No. 3.) 16mo, 0 50
—— Theory of Steel-concrete Arches and of Vaulted Structures. (Science Series No. 42.).....16mo, 0 50
—— Theory of Voussoir Arches. (Science Series No. 12.).....16mo, 0 50
—— Symbolic Algebra. (Science Series No. 73.).....16mo, 0 50
Carpenter, F. D. Geographical Surveying. (Science Series No. 37.).16mo,
Carpenter, R. C., and Diederichs, H. Internal Combustion Engines..8vo, *5 00
Carter, E. T. Motive Power and Gearing for Electrical Machinery.8vo, 3 50
Carter, H. A. Ramie (Rhea), China Grass.....12mo, *2 00
Carter, H. R. Modern Flax, Hemp, and Jute Spinning.....8vo, *3 00
—— Bleaching, Dyeing and Finishing of Fabrics.....8vo, *1 00
Cary, E. R. Solution of Railroad Problems with the Slide Rule..16mo, *1 00
Cathcart, W. L. Machine Design. Part I. Fastenings.....8vo, *3 00
Cathcart, W. L., and Chaffee, J. I. Elements of Graphic Statics...8vo, *3 00
—— Short Course in Graphics.....12mo, 1 50
Caven, R. M., and Lander, G. D. Systematic Inorganic Chemistry.12mo, *2 00
Chalkley, A. P. Diesel Engines.....8vo, *3 00
Chambers' Mathematical Tables.....8vo, 1 75
Chambers, G. F. Astronomy.....16mo, *1 50
Charpentier, P. Timber.....8vo, *6 00
Chatley, H. Principles and Designs of Aeroplanes. (Science Series No. 126).....16mo, 0 50
—— How to Use Water Power.....12mo, *1 00
—— Gyrostatic Balancing.....8vo, *1 00

Child, C. D. Electric Arc....8vo, *2 00
Child, C. T. The How and Why of Electricity....12mo, 1 00
Christian, M. Disinfection and Disinfectants. Trans. by Chas. Salter....12mo, 2 00
Christie, W. W. Boiler-waters, Scale, Corrosion, Foaming....8vo, *3 00
—— Chimney Design and Theory....8vo, *3 00
—— Furnace Draft. (Science Series No. 123.)....16mo, 0 50
—— Water: Its Purification and Use in the Industries....8vo, *2 00
Church's Laboratory Guide. Rewritten by Edward Kinch....8vo, *2 50
Clapperton, G. Practical Papermaking....8vo, 2 50
Clark, A. G. Motor Car Engineering.
Vol. I. Construction.... *3 00
Vol. II. Design.... (*In Press.*)
Clark, C. H. Marine Gas Engines....12mo, *1 50
Clark, J. M. New System of Laying Out Railway Turnouts....12mo, 1 00
Clarke, J. W., and Scott, W. Plumbing Practice.
Vol. I. Lead Working and Plumbers' Materials....8vo, *4 00
Vol. II. Sanitary Plumbing and Fittings....(*In Press.*)
Vol. III. Practical Lead Working on Roofs....(*In Press.*)
Clausen-Thue, W. A B C Telegraphic Code. Fourth Edition ...12mo, *5 00
Fifth Edition....8vo, *7 00
—— The A 1 Telegraphic Code....8vo, *7 50
Clerk, D., and Idell, F. E. Theory of the Gas Engine. (Science Series No. 62.)....16mo, 0 50
Clevenger, S. R. Treatise on the Method of Government Surveying. 16mo, morocco, 2 50
Clouth, F. Rubber, Gutta-Percha, and Balata....8vo, *5 00
Cochran, J. Concrete and Reinforced Concrete Specifications....8vo, *2 50
—— Inspection of Concrete Construction....8vo, *4 00
—— Treatise on Cement Specifications....8vo, *1 00
Coffin, J. H. C. Navigation and Nautical Astronomy....12mo, *3 50
Colburn, Z., and Thurston, R. H. Steam Boiler Explosions. (Science Series No. 2.)....16mo, 0 50
Cole, R. S. Treatise on Photographic Optics....12mo, 1 50
Coles-Finch, W. Water, Its Origin and Use....8vo, *5 00
Collins, J. E. Useful Alloys and Memoranda for Goldsmiths, Jewelers. 16mo, 0 50
Collis, A. G. High and Low Tension Switch-Gear Design....8vo, *3 50
—— Switchgear. (Installation Manuals Series.)....12mo, *0 50
Comstock, D. F., and Toland, L. T. Modern Theory of the Constitution of Matter....(*In Press.*)
Constantine, E. Marine Engineers, Their Qualifications and Duties. 8vo, *2 00
Coombs, H. A. Gear Teeth. (Science Series No. 120.)....16mo, 0 50
Cooper, W. R. Primary Batteries....8vo, *4 00
Copperthwaite, W. C. Tunnel Shields....4to, *9 00
Corey, H. T. Water Supply Engineering....8vo (*In Press.*)
Corfield, W. H. Dwelling Houses. (Science Series No. 50.)....16mo, 0 50
—— Water and Water-Supply. (Science Series No. 17.)....16mo, 0 50
Cornwall, H. B. Manual of Blow-pipe Analysis....8vo, *2 50

Courtney, C. F. Masonry Dams 8vo, 3 50
Cowell, W. B. Pure Air, Ozone, and Water 12mo, *2 00
Craig, J. W., and Woodward, W. P. Questions and Answers About Electrical Apparatus ..... 12mo, leather, 1 50
Craig, T. Motion of a Solid in a Fuel. (Science Series No. 49.) 16mo, 0 50
—— Wave and Vortex Motion. (Science Series No. 43.) 16mo, 0 50
Cramp, W. Continuous Current Machine Design 8vo, *2 50
Creedy, F. Single Phase Commutator Motors 8vo, *2 00
Crocker, F. B. Electric Lighting. Two Volumes. 8vo.
Vol. I. The Generating Plant 3 00
Vol. II. Distributing Systems and Lamps .....
Crocker, F. B., and Arendt, M. Electric Motors 8vo, *2 50
Crocker, F. B., and Wheeler, S. S. The Management of Electrical Machinery 12mo, *1 00
Cross, C. F., Bevan, E. J., and Sindall, R. W. Wood Pulp and Its Applications. (Westminster Series.) 8vo, *2 00
Crosskey, L. R. Elementary Perspective 8vo, 1 00
Crosskey, L. R., and Thaw, J. Advanced Perspective 8vo, 1 50
Culley, J. L. Theory of Arches. (Science Series No. 87.) 16mo, 0 50

Dadourian, H. M. Analytical Mechanics 12mo, *3 00
Dana, R. T. Handbook of Construction plant ..... 12mo, leather, *5 00
Danby, A. Natural Rock Asphalts and Bitumens 8vo, *2 50
Davenport, C. The Book. (Westminster Series.) 8vo, *2 00
Davey, N. The Gas Turbine 8vo, *4 00
Davies, F. H. Electric Power and Traction 8vo, *2 00
—— Foundations and Machinery Fixing. (Installation Manual Series.) 16mo, *1 00
Dawson, P. Electric Traction on Railways 8vo, *9 00
Deerr, N. Sugar Cane 8vo, *7 00
Deite, C. Manual of Soapmaking. Trans. by S. T. King 4to, *5 00
De la Coux, H. The Industrial Uses of Water. Trans. by A. Morris. 8vo, *4 50
Del Mar, W. A. Electric Power Conductors 8vo, *2 00
Denny, G. A. Deep-level Mines of the Rand 4to, *10 00
—— Diamond Drilling for Gold *5 00
De Roos, J. D. C. Linkages. (Science Series No. 47.) 16mo, 0 50
Derr, W. L. Block Signal Operation ..... Oblong 12mo, *1 50
—— Maintenance-of-Way Engineering ..... (*In Preparation.*)
Desaint, A. Three Hundred Shades and How to Mix Them 8vo, *8 00
De Varona, A. Sewer Gases. (Science Series No. 55.) 16mo, 0 50
Devey, R. G. Mill and Factory Wiring. (Installation Manuals Series.) 12mo, *1 00
Dibdin, W. J. Purification of Sewage and Water 8vo, 6 50
Dichmann, Carl. Basic Open-Hearth Steel Process 12mo, *3 50
Dieterich, K. Analysis of Resins, Balsams, and Gum Resins 8vo, *3 00
Dinger, Lieut. H. C. Care and Operation of Naval Machinery ... 12mo, *2 00
Dixon, D. B. Machinist's and Steam Engineer's Practical Calculator. 16mo, morocco, 1 25
Doble, W. A. Power Plant Construction on the Pacific Coast (*In Press.*)

Dodge, G. F. Diagrams for Designing Reinforced Concrete Structures, folio, *4 00
Dommett, W. E. Motor Car Mechanism.....12mo, *1 25
Dorr, B. F. The Surveyor's Guide and Pocket Table-book. 16mo, morocco, 2 00
Down, P. B. Handy Copper Wire Table.....16mo, *1 00
Draper, C. H. Elementary Text-book of Light, Heat and Sound..12mo, 1 00
—— Heat and the Principles of Thermo-dynamics.....12mo, *2 00
Dron, R. W. Mining Formulas.....12mo, 1 00
Dubbel, H. High Power Gas Engines.....8vo, *5 00
Duckwall, E. W. Canning and Preserving of Food Products.....8vo, *5 00
Dumesny, P., and Noyer, J. Wood Products, Distillates, and Extracts. 8vo, *4 50
Duncan, W. G., and Penman, D. The Electrical Equipment of Collieries. 8vo, *4 00
Dunstan, A. E., and Thole, F. B. T. Textbook of Practical Chemistry. 12mo, *1 40
Duthie, A. L. Decorative Glass Processes. (Westminster Series.).8vo, *2 00
Dwight, H. B. Transmission Line Formulas.....8vo, *2 00
Dyson, S. S. Practical Testing of Raw Materials.....8vo, *5 00
Dyson, S. S., and Clarkson, S. S. Chemical Works.....8vo, *7 50

Eccles, R. G., and Duckwall, E. W. Food Preservatives....8vo, paper, 0 50
Eccles, W. H. Wireless Telegraphy and Telephony.....(*In Press.*)
Eck, J. Light, Radiation and Illumination. Trans. by Paul Hogner, 8vo, *2 50
Eddy, H. T. Maximum Stresses under Concentrated Loads.....8vo, 1 50
Edelman, P. Inventions and Patents.....12mo. (*In Press.*)
Edgcumbe, K. Industrial Electrical Measuring Instruments.....8vo,
Edler, R. Switches and Switchgear. Trans. by Ph. Laubach...8vo, *4 00
Eissler, M. The Metallurgy of Gold.....8vo, 7 50
—— The Metallurgy of Silver.....8vo, 4 00
—— The Metallurgy of Argentiferous Lead.....8vo, 5 00
—— A Handbook on Modern Explosives.....8vo, 5 00
Ekin, T. C. Water Pipe and Sewage Discharge Diagrams .....folio, *3 00
Electric Light Carbons, Manufacture of.....8vo, 1 00
Eliot, C. W., and Storer, F. H. Compendious Manual of Qualitative Chemical Analysis.....12mo, *1 25
Ellis, C. Hydrogenation of Oils.....8vo, *4 00
Ellis, G. Modern Technical Drawing.....8vo, *2 00
Ennis, Wm. D. Linseed Oil and Other Seed Oils.....8vo, *4 00
—— Applied Thermodynamics.....8vo, *4 50
—— Flying Machines To-day.....12mo, *4 50
—— Vapors for Heat Engines.....12mo, *1 00
Erfurt, J. Dyeing of Paper Pulp. Trans. by J. Hubner.....
Ermen, W. F. A. Materials Used in Sizing 8vo, *2 00
Erwin, M. The Universe and the Atom.....(*In Press.*)
Evans, C. A. Macadamized Roads..... (*In Press.*)

Ewing, A. J. Magnetic Induction in Iron 8vo, *4 00

Fairie, J. Notes on Lead Ores 12mo, *1 00
—— Notes on Pottery Clays 12mo, *1 50
Fairley, W., and Andre, Geo. J. Ventilation of Coal Mines. (Science Series No. 58.) 16mo, 0 50
Fairweather, W. C. Foreign and Colonial Patent Laws 8vo, *3 00
Falk, M. S. Cement Mortars and Concretes 8vo, *2 50
Fanning, J. T. Hydraulic and Water-supply Engineering 8vo, *5 00
Fay, I. W. The Coal-tar Colors 8vo, *4 00
Fernbach, R. L. Glue and Gelatine 8vo, *3 00
—— Chemical Aspects of Silk Manufacture 12mo, *1 00
Fischer, E. The Preparation of Organic Compounds. Trans. by R. V. Stanford 12mo, *1 25
Fish, J. C. L. Lettering of Working Drawings ..... Oblong 8vo, 1 00
—— Mathematics of the Paper Location of a Railroad ..... paper, 12mo, *0 25
Fisher, H. K. C., and Darby, W. C. Submarine Cable Testing 8vo, *3 50
Fleischmann, W. The Book of the Dairy. Trans. by C. M. Aikman. 8vo, 4 00
Fleming, J. A. The Alternate-current Transformer. Two Volumes. 8vo.
Vol. I. The Induction of Electric Currents *5 00
Vol. II. The Utilization of Induced Currents *5 00
Fleming, J. A. Propagation of Electric Currents 8vo, *3 00
—— A Handbook for the Electrical Laboratory and Testing Room. Two Volumes ..... 8vo, each, *5 00
Fleury, P. Preparation and Uses of White Zinc Paints 8vo, *2 50
Flynn, P. J. Flow of Water. (Science Series No. 84.) 12mo, 0 50
—— Hydraulic Tables. (Science Series No. 66.) 16mo, 0 50
Forgie, J. Shield Tunneling ..... 8vo. (*In Press.*)
Foster, H. A. Electrical Engineers' Pocket-book. (*Seventh Edition.*) 12mo, leather, 5 00
—— Engineering Valuation of Public Utilities and Factories 8vo, *3 00
—— Handbook of Electrical Cost Data ..... 8vo (*In Press.*)
Foster, Gen. J. G. Submarine Blasting in Boston (Mass.) Harbor 4to, 3 50
Fowle, F. F. Overhead Transmission Line Crossings 12mo, *1 50
—— The Solution of Alternating Current Problems ..... 8vo (*In Press.*)
Fox, W. G. Transition Curves. (Science Series No. 110.) 16mo, 0 50
Fox, W., and Thomas, C. W. Practical Course in Mechanical Drawing 12mo, 1 25
Foye, J. C. Chemical Problems. (Science Series No. 69.) 16mo, 0 50
—— Handbook of Mineralogy. (Science Series No. 86.) 16mo, 0 50
Francis, J. B. Lowell Hydraulic Experiments 4to, 15 00
Franzen, H. Exercises in Gas Analysis 12mo, *1 00
French, J. W. Machine Tools, 2 vols 4to, *15 00
Freudemacher, P. W. Electrical Mining Installations. (Installation Manuals Series.) 12mo, *1 00
Frith, J. Alternating Current Design 8vo, *2 00
Fritsch, J. Manufacture of Chemical Manures. Trans. by D. Grant. 8vo, *4 00

Frye, A. I. Civil Engineers' Pocket-book.....12mo, leather, *5 00
Fuller, G. W. Investigations into the Purification of the Ohio River. 4to, *10 00
Furnell, J. Paints, Colors, Oils, and Varnishes.....8vo. *1 00

Gairdner, J. W. I. Earthwork.....8vo (*In Press.*)
Gant, L. W. Elements of Electric Traction.....8vo, *2 50
Garcia, A. J. R. V. Spanish-English Railway Terms.....8vo, *4 50
Garforth, W. E. Rules for Recovering Coal Mines after Explosions and Fires.....12mo, leather, 1 50
Garrard, C. C. Electric Switch and Controlling Gear....(*In Press.*)
Gaudard, J. Foundations. (Science Series No. 34.).....16mo, 0 50
Gear, H. B., and Williams, P. F. Electric Central Station Distribution Systems.....8vo, *3 00
Geerligs, H. C. P. Cane Sugar and Its Manufacture.....8vo, *5 00
Geikie, J. Structural and Field Geology.....8vo, *4 00
—— Mountains. Their Growth, Origin and Decay.....8vo, *4 00
—— The Antiquity of Man in Europe.....8vo, *3 00
Georgi, F., and Schubert, A. Sheet Metal Working. Trans. by C. Salter.....8vo, 3 00
Gerber, N. Analysis of Milk, Condensed Milk, and Infants' Milk-Food. 8vo, 1 25
Gerhard, W. P. Sanitation, Watersupply and Sewage Disposal of Country Houses.....12mo, *2 00
—— Gas Lighting (Science Series No. 111.).....16mo, 0 50
—— Household Wastes. (Science Series No. 97.).....16mo, 0 50
—— House Drainage. (Science Series No. 63.).....16mo, 0 50
Gerhard, W. P. Sanitary Drainage of Buildings. (Science Series No. 93.) 16mo, 0 50
Gerhardi, C. W. H. Electricity Meters.....8vo, *4 00
Geschwind, L. Manufacture of Alum and Sulphates. Trans. by C. Salter.....8vo, *5 00
Gibbs, W. E. Lighting by Acetylene.....12mo, *1 50
Gibson, A. H. Hydraulics and Its Application.....8vo, *5 00
—— Water Hammer in Hydraulic Pipe Lines.....12mo, *2 00
Gibson, A. H., and Ritchie, E. G. Circular Arc Bow Girder.....4to, *3 50
Gilbreth, F. B. Motion Study.....12mo, *2 00
—— Bricklaying System.....8vo, *3 00
—— Field System.....12mo, leather, *3 00
—— Primer of Scientific Management.....12mo, *1 00
Gillette, H. P. Handbook of Cost Data.....12mo, leather, *5 00
—— Rock Excavation Methods and Cost.....12mo, *3 00
—— and Dana, R. T. Cost Keeping and Management Engineering.8vo, *3 50
—— and Hill, C. S. Concrete Construction, Methods and Cost....8vo, *5 00
Gillmore, Gen. Q. A. Limes, Hydraulic Cements and Mortars.....8vo, 4 00
—— Roads, Streets, and Pavements.....12mo, 2 00
Godfrey, E. Tables for Structural Engineers.....16mo, leather, *2 50
Golding, H. A. The Theta-Phi Diagram.....12mo, *1 25
Goldschmidt, R. Alternating Current Commutator Motor.....8vo, *3 00
Goodchild, W. Precious Stones. (Westminster Series.).....8vo, *2 00

Goodeve, T. M. Textbook on the Steam-engine.. ..... 12mo, 2 00
Gore, G. Electrolytic Separation of Metals..... 8vo, *3 50
Gould, E. S. Arithmetic of the Steam-engine..... 12mo, 1 00
—— Calculus. (Science Series No. 112.)..... 16mo, 0 50
—— High Masonry Dams. (Science Series No. 22.)..... 16mo, 0 50
—— Practical Hydrostatics and Hydrostatic Formulas. (Science Series No. 117.)..... 16mo, 0 50
Gratacap, L. P. A Popular Guide to Minerals..... 8vo, *3 00
Gray, J. Electrical Influence Machines..... 12mo, 2 00
—— Marine Boiler Design..... 12mo, *1 25
Greenhill, G. Dynamics of Mechanical Flight..... 8vo, *2 50
Greenwood, E. Classified Guide to Technical and Commercial Books. 8vo, *3 00
Gregorius, R. Mineral Waxes. Trans. by C. Salter..... 12mo, *3 00
Griffiths, A. B. A Treatise on Manures..... 12mo, 3 00
—— Dental Metallurgy..... 8vo, *3 50
Gross, E. Hops..... 8vo, *4 50
Grossman, J. Ammonia and Its Compounds..... 12mo, *1 25
Groth, L. A. Welding and Cutting Metals by Gases or Electricity. (Westminster Series)..... 8vo, *2 00
Grover, F. Modern Gas and Oil Engines..... 8vo, *2 00
Gruner, A. Power-loom Weaving..... 8vo, *3 00
Güldner, Hugo. Internal Combustion Engines. Trans. by H. Diederichs. 4to, *10 00
Gunther, C. O. Integration.....
Gurden, R. L. Traverse Tables..... folio, half morocco, *7 50
Guy, A. E. Experiments on the Flexure of Beams..... 8vo, *1 25

Haenig, A. Emery and Emery Industry..... 8vo, *2 50
Hainbach, R. Pottery Decoration. Trans. by C. Salter..... 12mo, *3 00
Hale, W. J. Calculations of General Chemistry..... 12mo, *1 00
Hall, C. H. Chemistry of Paints and Paint Vehicles..... 12mo, *2 00
Hall, G. L. Elementary Theory of Alternate Current Working.... 8vo, *1 50
Hall, R. H. Governors and Governing Mechanism..... 12mo, *2 00
Hall, W. S. Elements of the Differential and Integral Calculus..... 8vo, *2 25
—— Descriptive Geometry ..... 8vo volume and a 4to atlas, *3 50
Haller, G. F., and Cunningham, E. T. The Tesla Coil..... 12mo, *1 25
Halsey, F. A. Slide Valve Gears..... 12mo, 1 50
—— The Use of the Slide Rule. (Science Series No. 114.)..... 16mo, 0 50
—— Worm and Spiral Gearing. (Science Series No. 116.)..... 16mo, 0 50
Hamilton, W. G. Useful Information for Railway Men..... 16mo, 1 00
Hammer, W. J. Radium and Other Radio-active Substances..... 8vo, *1 00
Hancock, H. Textbook of Mechanics and Hydrostatics..... 8vo, 1 50
Hancock, W. C. Refractory Materials. (Metallurgy Series.) (*In Press.*)
Hardy, E. Elementary Principles of Graphic Statics..... 12mo, *1 50
Haring, H. Engineering Law.
Vol. I. Law of Contract..... 8vo, *4 00
Harris, S. M. Practical Topographical Surveying..... (*In Press.*)
Harrison, W. B. The Mechanics' Tool-book..... 12mo, 1 50
Hart, J. W. External Plumbing Work..... 8vo, *3 00
—— Hints to Plumbers on Joint Wiping..... 8vo, *3 00

—— Principles of Hot Water Supply....8vo, *3 00
—— Sanitary Plumbing and Drainage....8vo, *3 00
Haskins, C. H. The Galvanometer and Its Uses....16mo, 1 50
Hatt, J. A. H. The Colorist....square 12mo, *1 50
Hausbrand, E. Drying by Means of Air and Steam. Trans. by A. C. Wright....12mo, *2 00
—— Evaporating, Condensing and Cooling Apparatus. Trans. by A. C. Wright....8vo, *5 00
Hausmann, E. Telegraph Engineering....8vo, *3 00
Hausner, A. Manufacture of Preserved Foods and Sweetmeats. Trans. by A. Morris and H. Robson....8vo, *3 00
Hawkesworth, J. Graphical Handbook for Reinforced Concrete Design. 4to, *2 50
Hay, A. Alternating Currents....8vo, *2 50
—— Electrical Distributing Networks and Distributing Lines....8vo, *3 50
—— Continuous Current Engineering....8vo, *2 50
Hayes, H. V. Public Utilities, Their Cost New and Depreciation...8vo, *2 00
—— Public Utilities, Their Fair Present Value and Return....8vo, *2 00
Heather, H. J. S. Electrical Engineering....8vo, *3 50
Heaviside, O. Electromagnetic Theory. Vols. I and II....8vo, each, *5 00
Vol. III....8vo, *7 50
Heck, R. C. H. The Steam Engine and Turbine....8vo, *3 50
—— Steam-Engine and Other Steam Motors. Two Volumes.
Vol. I. Thermodynamics and the Mechanics....8vo, *3 50
Vol. II. Form, Construction, and Working....8vo, *5 00
—— Notes on Elementary Kinematics....8vo, boards, *1 00
—— Graphics of Machine Forces....8vo, boards, *1 00
Heermann, P. Dyers' Materials. Trans. by A. C. Wright....12mo, *2 50
Heidenreich, E. L. Engineers' Pocketbook of Reinforced Concrete, 16mo, leather, *3 00
Hellot, Macquer and D'Apligny. Art of Dyeing Wool, Silk and Cotton. 8vo, *2 00
Henrici, O. Skeleton Structures....8vo, 1 50
Hering, D. W. Essentials of Physics for College Students....8vo, *1 75
Hering-Shaw, A. Domestic Sanitation and Plumbing. Two Vols...8vo, *5 00
Hering-Shaw, A. Elementary Science....8vo, *2 00
Herrmann, G. The Graphical Statics of Mechanism. Trans. by A. P. Smith....12mo, 2 00
Herzfeld, J. Testing of Yarns and Textile Fabrics....8vo, *3 50
Hildebrandt, A. Airships, Past and Present....8vo, *3 50
Hildenbrand, B. W. Cable-Making. (Science Series No. 32.)....16mo, 0 50
Hilditch, T. P. A Concise History of Chemistry....12mo, *1 25
Hill, C. S. Concrete Inspection....16mo, *1 00
Hill, J. W. The Purification of Public Water Supplies. New Edition. (*In Press.*)
—— Interpretation of Water Analysis....(*In Press.*)
Hill, M. J. M. The Theory of Proportion....8vo, *2 50
Hiroi, I. Plate Girder Construction. (Science Series No. 95.)...16mo, 0 50
—— Statically-Indeterminate Stresses....12mo, *2 00
Hirshfeld, C. F. Engineering Thermodynamics. (Science Series No. 45.) 16mo, 0 50

Hobart, H. M. Heavy Electrical Engineering....8vo, *4 50
—— Design of Static Transformers....12mo, *2 00
—— Electricity....8vo, *2 00
—— Electric Trains....8vo, *2 50
Hobart, H. M. Electric Propulsion of Ships....8vo, *2 00
Hobart, J. F. Hard Soldering, Soft Soldering and Brazing....12mo, *1 00
Hobbs, W. R. P. The Arithmetic of Electrical Measurements....12mo, 0 50
Hoff, J. N. Paint and Varnish Facts and Formulas....12mo, *1 50
Hole, W. The Distribution of Gas....8vo, *7 50
Holley, A. L. Railway Practice....folio, 6 00
Holmes, A. B. The Electric Light Popularly Explained...12mo, paper, 0 50
Hopkins, N. M. Experimental Electrochemistry....8vo,
—— Model Engines and Small Boats....12mo, 1 25
Hopkinson, J., Shoolbred, J. N., and Day, R. E. Dynamic Electricity. (Science Series No. 71.)....16mo, 0 50
Horner, J. Practical Ironfounding....8vo, *2 00
—— Gear Cutting, in Theory and Practice....8vo, *3 00
Houghton, C. E. The Elements of Mechanics of Materials....12mo, *2 00
Houllevigue, L. The Evolution of the Sciences....8vo, *2 00
Houstoun, R. A. Studies in Light Production....12mo, 2 00
Hovenden, F. Practical Mathematics for Young Engineers....12mo, *1 00
Howe, G. Mathematics for the Practical Man....12mo, *1 25
Howorth, J. Repairing and Riveting Glass, China and Earthenware. 8vo, paper, *0 50
Hubbard, E. The Utilization of Wood-waste....8vo, *2 50
Hübner, J. Bleaching and Dyeing of Vegetable and Fibrous Materials. (Outlines of Industrial Chemistry.)....8vo, *5 00
Hudson, O. F. Iron and Steel. (Outlines of Industrial Chemistry.)....8vo, *2 00
Humphrey, J. C. W. Metallography of Strain. (Metallurgy Series.) (*In Press.*)
Humphreys, A. C. The Business Features of Engineering Practice....8vo, *1 25
Hunter, A. Bridge Work....8vo. (*In Press.*)
Hurst, G. H. Handbook of the Theory of Color....8vo, *2 50
—— Dictionary of Chemicals and Raw Products....8vo, *3 00
—— Lubricating Oils, Fats and Greases....8vo, *4 00
—— Soaps....8vo, *5 00
Hurst, G. H., and Simmons, W. H. Textile Soaps and Oils....8vo, *2 50
Hurst, H. E., and Lattey, R. T. Text-book of Physics....8vo, *3 00
—— Also published in three parts.
Part I. Dynamics and Heat.... *1 25
Part II. Sound and Light.... *1 25
Part III. Magnetism and Electricity.... *1 50
Hutchinson, R. W., Jr. Long Distance Electric Power Transmission. 12mo, *3 00
Hutchinson, R. W., Jr., and Thomas, W. A. Electricity in Mining. 12mo, (*In Press.*)
Hutchinson, W. B. Patents and How to Make Money Out of Them. 12mo, 1 25
Hutton, W. S. Steam-boiler Construction....8vo, 6 00
—— The Works' Manager's Handbook....8vo, 6 00

Hyde, E. W. Skew Arches. (Science Series No. 15.) 16mo, 0 50
Hyde, F. S. Solvents, Oils, Gums, Waxes 8vo, *2 00

Induction Coils. (Science Series No. 53.) 16mo, 0 50
Ingham, A. E. Gearing. A practical treatise 8vo, *2 50
Ingle, H. Manual of Agricultural Chemistry 8vo, *3 00
Inness, C. H. Problems in Machine Design 12mo, *2 00
—— Air Compressors and Blowing Engines 12mo, *2 00
—— Centrifugal Pumps 12mo, *2 00
—— The Fan 12mo, *2 00
Isherwood, B. F. Engineering Precedents for Steam Machinery ... 8vo, 2 50
Ivatts, E. B. Railway Management at Stations 8vo, *2 50

Jacob, A., and Gould, E. S. On the Designing and Construction of Storage Reservoirs. (Science Series No. 6) 16mo, 0 50
Jannettaz, E. Guide to the Determination of Rocks. Trans. by G. W. Plympton 12mo, 1 50
Jehl, F. Manufacture of Carbons 8vo, *4 00
Jennings, A. S. Commercial Paints and Painting. (Westminster Series.) 8vo, *2 00
Jennison, F. H. The Manufacture of Lake Pigments 8vo, *3 00
Jepson, G. Cams and the Principles of their Construction 8vo, *1.50
—— Mechanical Drawing ..... 8vo (*In Preparation.*)
Jervis-Smith, F. J. Dynamometers 8vo, *3 50
Jockin, W. Arithmetic of the Gold and Silversmith 12mo, *1 00
Johnson, J. H. Arc Lamps and Accessory Apparatus. (Installation Manuals Series.) 12mo, *0 75
Johnson, T. M. Ship Wiring and Fitting. (Installation Manuals Series.) 12mo, *0 75
Johnson, W. McA. The Metallurgy of Nickel ..... (*In Preparation.*)
Johnston, J. F. W., and Cameron, C. Elements of Agricultural Chemistry and Geology 12mo, 2 60
Joly, J. Radioactivity and Geology 12mo, 3 00
Jones, H. C. Electrical Nature of Matter and Radioactivity 12mo, *2 00
—— Evolution of Solutions ..... (*In Press.*)
—— New Era in Chemistry 12mo, *2 00
Jones, J. H. Tinplate Industry 8vo, *3 00
Jones, M. W. Testing Raw Materials Used in Paint 12mo, *2 00
Jordan, L. C. Practical Railway Spiral ..... 12mo, leather, *1 50
Joynson, F. H. Designing and Construction of Machine Gearing .. 8vo, 2 00
Jüptner, H. F. V. Siderology: The Science of Iron 8vo, *5 00

Kansas City Bridge 4to, 6 00
Kapp, G. Alternate Current Machinery. (Science Series No. 96.) .. 16mo, 0 50
Keim, A. W. Prevention of Dampness in Buildings 8vo, *2 00
Keller, S. S. Mathematics for Engineering Students. 12mo, half leather.
Algebra and Trigonometry, with a Chapter on Vectors *1 75
Plane and Solid Geometry *1.25
—— and Knox, W. E. Analytical Geometry and Calculus *2 00
Kelsey, W. R. Continuous-current Dynamos and Motors 8vo, *2 50

Kemble, W. T., and Underhill, C. R. The Periodic Law and the Hydrogen Spectrum ..... 8vo, paper, *0 50
Kemp, J. F. Handbook of Rocks 8vo, *1 50
Kendall, E. Twelve Figure Cipher Code 4to, *12 50
Kennedy, A. B. W., and Thurston, R. H. Kinematics of Machinery. (Science Series No. 54.) 16mo, 0 50
Kennedy, A. B. W., Unwin, W. C., and Idell, F. E. Compressed Air. (Science Series No. 106.) 16mo, 0 50
Kennedy, R. Modern Engines and Power Generators. Six Volumes. 4to, 15 00
Single Volumes ..... each, 3 00
—— Electrical Installations. Five Volumes 4to, 15 00
Single Volumes ..... each, 3 50
—— Flying Machines; Practice and Design 12mo, *2 00
—— Principles of Aeroplane Construction 8vo, *1 50
Kennelly, A. E. Electro-dynamic Machinery 8vo, 1 50
Kent, W. Strength of Materials. (Science Series No. 41.) 16mo, 0 50
Kershaw, J. B. C. Fuel, Water and Gas Analysis 8vo, *2 50
—— Electrometallurgy. (Westminster Series.) 8vo, *2 00
—— The Electric Furnace in Iron and Steel Production 12mo, *1 50
—— Electro-Thermal Methods of Iron and Steel Production 8vo, *3 00
Kindelan, J. Trackman's Helper 12mo, *1 50
Kinzbrunner, C. Alternate Current Windings 8vo, *1 50
—— Continuous Current Armatures 8vo, *1 50
—— Testing of Alternating Current Machines 8vo, *2 00
Kirkaldy, W. G. David Kirkaldy's System of Mechanical Testing 4to, 10 00
Kirkbride, J. Engraving for Illustration 8vo, *1 50
Kirkham, J. E. Structural Engineering 8vo, *5 00
Kirkwood, J. P. Filtration of River Waters 4to, 7 50
Kirschke, A. Gas and Oil Engines 12mo, *1 25
Klein, J. F. Design of a High-speed Steam-engine 8vo, *5 00
—— Physical Significance of Entropy 8vo, *1 50
Kleinhans, F. B. Boiler Construction 8vo, 3 00
Knight, R.-Adm. A. M. Modern Seamanship 8vo, *7 50
Half morocco *9 00
Knott, C. G., and Mackay, J. S. Practical Mathematics 8vo, 2 00
Knox, J. Physico-Chemical Calculations 12mo, *1 00
—— Fixation of Atmospheric Nitrogen. (Chemical Monographs.) 12mo, *0 75
Koester, F. Steam-Electric Power Plants 4to, *5 00
—— Hydroelectric Developments and Engineering 4to, *5 00
Koller, T. The Utilization of Waste Products 8vo, *3 00
—— Cosmetics 8vo, *2 50
Kremann, R. Application of the Physico-Chemical Theory to Technical Processes and Manufacturing Methods. Trans. by H. E. Potts 8vo, *2 50
Kretchmar, K. Yarn and Warp Sizing 8vo, *4 00

Lallier, E. V. Elementary Manual of the Steam Engine 12mo, *2 00
Lambert, T. Lead and Its Compounds 8vo, *3 50
—— Bone Products and Manures 8vo, *3 00

Lamborn, L. L. Cottonseed Products....8vo, *3 00
—— Modern Soaps, Candles, and Glycerin....8vo, *7 50
Lamprecht, R. Recovery Work After Pit Fires. Trans. by C. Salter.8vo, *4 00
Lancaster, M. Electric Cooking, Heating and Cleaning....8vo, *1 50
Lanchester, F. W. Aerial Flight. Two Volumes. 8vo.
Vol. I. Aerodynamics.... *6 00
—— Aerial Flight. Vol. II. Aerodonetics.... *6.00
Lange, K. R. By-Products of Coal-Gas Manufacture....12mo, 2 00
Larner, E. T. Principles of Alternating Currents....12mo. *1 25
La Rue, B. F. Swing Bridges. (Science Series No. 107.)....16mo, 0 50
Lassar-Cohn. Dr. Modern Scientific Chemistry. Trans. by M. M. Pattison Muir....12mo, *2 00
Latimer, L. H., Field, C. J., and Howell, J. W. Incandescent Electric Lighting. (Science Series No. 57.)....16mo, 0 50
Latta, M. N. Handbook of American Gas-Engineering Practice...8vo, *4 50
—— American Producer Gas Practice....4to, *6 00
Laws, B. C. Stability and Equilibrium of Floating Bodies....8vo, *3 50
Lawson, W. R. British Railways. A Financial and Commercial Survey....8vo, 2 00
Leask, A. R. Breakdowns at Sea....12mo, 2 00
—— Refrigerating Machinery....12mo, 2 00
Lecky, S. T. S. "Wrinkles" in Practical Navigation....8vo, *8 00
Le Doux, M. Ice-Making Machines. (Science Series No. 46.)..16mo, 0 50
Leeds, C. C. Mechanical Drawing for Trade Schools. (Machinery Trades Edition.)....oblong 4to *2 00
—— Mechanical Drawing for High and Vocational Schools....4to, *1 50
Lefévre, L. Architectural Pottery. Trans. by H. K. Bird and W. M. Binns....4to, *7 50
Lehner, S. Ink Manufacture. Trans. by A. Morris and H. Robson.8vo, *2 50
Lemstrom, S. Electricity in Agriculture and Horticulture....8vo, *1 50
Letts, E. A. Fundamental Problems in Chemistry....8vo, *2 00
Le Van, W. B. Steam-Engine Indicator. (Science Series No. 78.)16mo, 0 50
Lewes, V. B. Liquid and Gaseous Fuels. (Westminster Series.)..8vo, *2 00
—— Carbonization of Coal....8vo, *3 00
Lewis, L. P. Railway Signal Engineering....8vo, *3 50
Lieber, B. F. Lieber's Standard Telegraphic Code....8vo, *10 00
—— Code. German Edition....8vo, *10 00
—— —— Spanish Edition....8vo, *10 00
—— —— French Edition....8vo, *10 00
—— Terminal Index....8vo, *2 50
—— Lieber's Appendix....folio, *15 00
—— —— Handy Tables....4to, *2 50
—— Bankers and Stockbrokers' Code and Merchants and Shippers' Blank Tables....8vo, *15 00
—— 100,000,000 Combination Code....8vo, *10 00
—— Engineering Code....8vo, *12 50
Livermore, V. P., and Williams, J. How to Become a Competent Motorman....12mo, *1 00
Livingstone, R. Design and Construction of Commutators....8vo, *2 25
—— Mechanical Design and Construction of Generators....8vo, *3 50
Lobben, P. Machinists' and Draftsmen's Handbook....8vo, 2 50

Lockwood, T. D. Electricity, Magnetism, and Electro-telegraph....8vo, 2 50

Lockwood, T. D. Electrical Measurement and the Galvanometer. 12mo, 0 75

Lodge, O. J. Elementary Mechanics....12mo, 1 50

—— Signalling Across Space without Wires....8vo, *2 00

Loewenstein, L. C., and Crissey, C. P. Centrifugal Pumps.... *4 50

Lomax, J. W. Cotton Spinning....12mo, 1 50

Lord, R. T. Decorative and Fancy Fabrics....8vo, *3 50

Loring, A. E. A Handbook of the Electromagnetic Telegraph....16mo 0 50

—— Handbook. (Science Series No. 39.)....16m, 0 50

Lovell, D. H. Practical Switchwork....12mo, *1 00

Low, D. A. Applied Mechanics (Elementary)....16mo, 0 80

Lubschez, B. J. Perspective....12mo, *1 50

Lucke, C. E. Gas Engine Design....8vo, *3 00

—— Power Plants: Design, Efficiency, and Power Costs. 2 vols. (*In Preparation.*)

Luckiesh, M. Color and Its Application....8vo. (*In Press.*)

Lunge, G. Coal-tar and Ammonia. Two Volumes....8vo, *15 00

—— Technical Gas Analysis....8vo, *4 00

—— Manufacture of Sulphuric Acid and Alkali. Four Volumes....8vo,

Vol. I. Sulphuric Acid. In three parts....*18 00

Vol. II. Salt Cake, Hydrochloric Acid and Leblanc Soda. In two parts....*15.00

Vol. III. Ammonia Soda....*10 00

Vol. IV. Electrolytic Methods....(*In Press.*)

—— Technical Chemists' Handbook....12mo, leather, *3 50

—— Technical Methods of Chemical Analysis. Trans. by C. A. Keane in collaboration with the corps of specialists.

Vol. I. In two parts....8vo, *15 00

Vol. II. In two parts....8vo, *18 00

Vol. III. In two parts....8vo, *18 00

The set (3 vols.) complete.... *48 00

Luquer, L. M. Minerals in Rock Sections....8vo, *1 50

Macaulay, J., and Hall, C. Modern Railway Working, 8 vols....4to, 20 00

Each volume separately.... 3 00

Macewen, H. A. Food Inspection....8vo, *2 50

Mackenzie, N. F. Notes on Irrigation Works....8vo, *2 50

Mackie, J. How to Make a Woolen Mill Pay....8vo, *2 00

Mackrow, C. Naval Architect's and Shipbuilder's Pocket-book. 16mo, leather, 5 00

Maguire, Wm. R. Domestic Sanitary Drainage and Plumbing....8vo, 4 00

Malcolm, C. W. Textbook on Graphic Statics....8vo, *3 00

Malcolm, H. W. Submarine Telegraph Cable....(*In Press.*)

Mallet, A. Compound Engines. Trans. by R. R. Buel. (Science Series No. 10.)....16mo,

Mansfield, A. N. Electro-magnets. (Science Series No. 64.)....16mo, 0 50

Marks, E. C. R. Construction of Cranes and Lifting Machinery.12mo, *1 50

—— Construction and Working of Pumps....12mo, *1 50

—— Manufacture of Iron and Steel Tubes 12mo, *2 00
—— Mechanical Engineering Materials 12mo, *1 00
Marks, G. C. Hydraulic Power Engineering 8vo, 3 50
—— Inventions, Patents and Designs 12mo, *1 00
Marlow, T. G. Drying Machinery and Practice 8vo, *5 00
Marsh, C. F. Concise Treatise on Reinforced Concrete 8vo, *2 50
—— Reinforced Concrete Compression Member Diagram. Mounted on Cloth Boards *1.50
Marsh, C. F., and Dunn, W. Manual of Reinforced Concrete and Concrete Block Construction ..... 16mo, morocco, *2 50
Marshall, W. J., and Sankey, H. R. Gas Engines. (Westminster Series.) 8vo, *2 00
Martin, G. Triumphs and Wonders of Modern Chemistry 8vo, *2 00
—— Modern Chemistry and Its Wonders ..... (*In Press.*)
Martin, N. Properties and Design of Reinforced Concrete 12mo, *2 50
Martin, W. D. Hints to Engineers 12mo, *1 00
Massie, W. W., and Underhill, C. R. Wireless Telegraphy and Telephony. 12mo, *1 00
Matheson, D. Australian Saw-Miller's Log and Timber Ready Reckoner. 12mo, leather, 1 50
Mathot, R. E. Internal Combustion Engines 8vo, *6 00
Maurice, W. Electric Blasting Apparatus and Explosives 8vo, *3 50
—— Shot Firer's Guide 8vo, *1 50
Maxwell, J. C. Matter and Motion. (Science Series No. 36.). 16mc, 0 50
Maxwell, W. H., and Brown, J. T. Encyclopedia of Municipal and Sanitary Engineering 4to, *10 00
Mayer, A. M. Lecture Notes on Physics 8vo, 2 00
Mayer, C., and Slippy, J. C. Telephone Line Construction 8vo, *3 00
McCullough, E. Practical Surveying 12mo, *2 00
—— Engineering Work in Cities and Towns 8vo, *3 00
—— Reinforced Concrete 12mo, *1 50
McCullough, R. S. Mechanical Theory of Heat 8vo, 3 50
McGibbon, W. C. Indicator Diagrams for Marine Engineers 8vo, *3 00
—— Marine Engineers' Drawing Book ..... oblong 4to, *2 00
McIntosh, J. G. Technology of Sugar 8vo, *4 50
—— Industrial Alcohol 8vo, *3 00
—— Manufacture of Varnishes and Kindred Industries. Three Volumes. 8vo.
Vol. I. Oil Crushing, Refining and Boiling *3 50
Vol. II. Varnish Materials and Oil Varnish Making *4 00
Vol. III. Spirit Varnishes and Materials *4 50
McKnight, J. D., and Brown, A. W. Marine Multitubular Boilers *1 50
McMaster, J. B. Bridge and Tunnel Centres. (Science Series No. 20.) 16mo, 0 50
McMechen, F. L. Tests for Ores, Minerals and Metals 12mo, *1 00
McPherson, J. A. Water-works Distribution 8vo, 2 50
Meade, R. K. Design and Equipment of Small Chemical Laboratories, 8vo,
Melick, C. W. Dairy Laboratory Guide 12mo, *1 25

Mensch, L. J. Reinforced Concrete Pocket Book.....16mo, leather, *4 00
Merck, E. Chemical Reagents; Their Purity and Tests. Trans. by H. E. Schenck.....8vo, 1 00
Merivale, J. H. Notes and Formulae for Mining Students.....12mo, 1 50
Merritt, Wm. H. Field Testing for Gold and Silver.....16mo, leather, 1 50
Meyer, J. G. A., and Pecker, C. G. Mechanical Drawing and Machine Design.....4to, 5 00
Mierzinski, S. Waterproofing of Fabrics. Trans. by A. Morris and H. Robson.....8vo, *2 50
Miessner, B. F. Radio Dynamics.....(*In Prcss.*)
Miller, G. A. Determinants. (Science Series No 105.).....16mo,
Milroy, M. E. W. Home Lace-making.....12mo, *1 00
Mitchell, C. A. Mineral and Aerated Waters.....8vo, *3 00
Mitchell, C. A., and Prideaux, R. M. Fibres Used in Textile and Allied Industries.....8vo, *3 00
Mitchell, C. F., and G. A. Building Construction and Drawing. 12mo.
Elementary Course..... *1 50
Advanced Course..... *2 50
Monckton, C. C. F. Radiotelegraphy. (Westminster Series.).....8vo, *2 00
Monteverde, R. D. Vest Pocket Glossary of English-Spanish, Spanish-English Technical Terms.....64mo, leather, *1 00
Montgomery, J. H. Electric Wiring Specifications.....16mo, *1 00
Moore, E. C. S. New Tables for the Complete Solution of Ganguillet and Kutter's Formula.....8vo, *5 00
Morecroft, J. H., and Hehre, F. W. Short Course in Electrical Testing. 8vo, *1 50
Morgan, A. P. Wireless Telegraph Apparatus for Amateurs.....12mo, *1 50
Moses, A. J. The Characters of Crystals.....8vo, *2 00
—— and Parsons, C. L. Elements of Mineralogy.....8vo, *2 50
Moss, S.A. Elements of Gas Engine Design. (Science Series No.121.)16mo, 0 50
—— The Lay-out of Corliss Valve Gears. (Science Series No. 119.)16mo, 0 50
Mulford, A. C. Boundaries and Landmarks.....12mo, *1 00
Mullin, J. P. Modern Moulding and Pattern-making.....12mo, 2 50
Munby, A. E. Chemistry and Physics of Building Materials. (Westminster Series.).....8vo, *2 00
Murphy, J. G. Practical Mining.....16mo, 1 00
Murphy, W. S. Textile Industries. Eight Volumes..... *20 00
Sold separately, each, *3 00
Murray, J. A. Soils and Manures. (Westminster Series.).....8vo, *2 00

Naquet, A. Legal Chemistry.....12mo, 2 00
Nasmith, J. The Student's Cotton Spinning.....8vo, 3 00
—— Recent Cotton Mill Construction.....12mo, 2 00
Neave, G. B., and Heilbron, I. M. Identification of Organic Compounds. 12mo, *1 25
Neilson, R. M. Aeroplane Patents.....8vo, *2 00
Nerz, F. Searchlights. Trans. by C. Rodgers.....8vo, *3 00
Neuberger, H., and Noalhat, H. Technology of Petroleum. Trans. by J. G. McIntosh.....8vo, *10 00
Newall, J. W. Drawing, Sizing and Cutting Bevel-gears.....8vo, 1 50

Newbeging, T. Handbook for Gas Engineers and Managers.....8vo, *6 50
Newton, G. J. Underground Distribution Systems.....(*In Press.*)
Nicol, G. Ship Construction and Calculations.....8vo, *4 50
Nipher, F. E. Theory of Magnetic Measurements.....12mo, 1 00
Nisbet, H. Grammar of Textile Design.....8vo, *3 00
Nolan, H. The Telescope. (Science Series No. 51.).....16mo, 0 50
Noll, A. How to Wire Buildings.....12mo, 1 50
North, H. B. Laboratory Experiments in General Chemistry.....12mo, *1 00
Nugent, E. Treatise on Optics.....12mo, 1 50

O'Connor, H. The Gas Engineer's Pocketbook.....12mo, leather, 3 50
—— Petrol Air Gas.....12mo, *0 75
Ohm, G. S., and Lockwood, T. D. Galvanic Circuit. Translated by William Francis. (Science Series No. 102.).....16mo, 0 50
Olsen, J. C. Text-book of Quantitative Chemical Analysis.....8vo, *4 00
Olsson, A. Motor Control, in Turret Turning and Gun Elevating. (U. S. Navy Electrical Series, No. 1.).....12mo, paper, *0 50
Ormsby, M. T. M. Surveying.....12mo, 1 50
Oudin, M. A. Standard Polyphase Apparatus and Systems.....8vo, *3 00
Owen, D. Recent Physical Research.....8vo, *1 50

Pakes, W. C. C., and Nankivell, A. T. The Science of Hygiene..8vo, *1 75
Palaz, A. Industrial Photometry. Trans. by G. W. Patterson, Jr..8vo, *4 00
Pamely, C. Colliery Manager's Handbook.....8vo, *10 00
Parker, P. A. M. The Control of Water.....8vo, *5 00
Parr, G. D. A. Electrical Engineering Measuring Instruments....8vo, *3 50
Parry, E. J. Chemistry of Essential Oils and Artificial Perfumes...8vo, *5 00
—— Foods and Drugs. Two Volumes.....8vo,
Vol. I. Chemical and Microscopical Analysis of Foods and Drugs. *7 50
Vol. II. Sale of Food and Drugs Act..... *3 00
—— and Coste, J. H. Chemistry of Pigments.....8vo, *4 50
Parry, L. Notes on Alloys.....8vo, *3 00
—— Metalliferous Wastes.....8vo, *2 00
—— Analysis of Ashes and Alloys.....8vo, *2 00
Parry, L. A. Risk and Dangers of Various Occupations.....8vo, *3 00
Parshall, H. F., and Hobart, H. M. Armature Windings.....4to, *7 50
—— Electric Railway Engineering.....4to, *10 00
Parsons, J. L. Land Drainage.....8vo, *1 50
Parsons, S. J. Malleable Cast Iron.....8vo, *2 50
Partington, J. R. Higher Mathematics for Chemical Students..12mo, *2 00
—— Textbook of Thermodynamics.....8vo, *4 00
Passmore, A. C. Technical Terms Used in Architecture.....8vo, *3 50
Patchell, W. H. Electric Power in Mines.....8vo, *4 00
Paterson, G. W. L. Wiring Calculations.....12mo, *2 00
—— Electric Mine Signalling Installations.....12mo, *1 50
Patterson, D. The Color Printing of Carpet Yarns.....8vo, *3 50
—— Color Matching on Textiles.....8vo, *3 00
—— Textile Color Mixing.....8vo, *3 00
Paulding, C. P. Condensation of Steam in Covered and Bare Pipes..8vo, *2 00
—— Transmission of Heat through Cold-storage Insulation.....12mo, *1 00

Payne, D. W. Iron Founders' Handbook.....(*In Press.*)
Peckham, S. F. Solid Bitumens.....8vo, *5 00
Peddie, R. A. Engineering and Metallurgical Books.....12mo, *1 50
Peirce, B. System of Analytic Mechanics.....4to, 10 00
Pendred, V. The Railway Locomotive. (Westminster Series.).....8vo, *2 00
Perkin, F. M. Practical Methods of Inorganic Chemistry.....12mo, *1 00
—— and Jaggers, E. M. Elementary Chemistry.....12mo, *1 00
Perrigo, O. E. Change Gear Devices.....8vo, 1 00
Perrine, F. A. C. Conductors for Electrical Distribution.....8vo, *3 50
Petit, G. White Lead and Zinc White Paints.....8vo, *1 50
Petit, R. How to Build an Aeroplane. Trans. by T. O'B. Hubbard, and J. H. Ledeboer.....8vo, *1 50
Pettit, Lieut. J. S. Graphic Processes. (Science Series No. 76.)...16mo, 0 50
Philbrick, P. H. Beams and Girders. (Science Series No. 88.)...16mo,
Phillips, J. Gold Assaying.....8vo, *2 50
—— Dangerous Goods.....8vo, 3 50
Phin, J. Seven Follies of Science.....12mo, *1 25
Pickworth, C. N. The Indicator Handbook. Two Volumes..12mo, each, 1 50
—— Logarithms for Beginners.....12mo. boards, 0 50
—— The Slide Rule.....12mo, 1 00
Plattner's Manual of Blow-pipe Analysis. Eighth Edition, revised. Trans. by H. B. Cornwall.....8vo, *4 00
Plympton, G. W. The Aneroid Barometer. (Science Series No. 35.) 16mo, 0 50
—— How to become an Engineer. (Science Series No. 100.).....16mo, 0 50
—— Van Nostrand's Table Book. (Science Series No. 104.).....16mo, 0 50
Pochet, M. L. Steam Injectors. Translated from the French. (Science Series No. 29.).....16mo, 0 50
Pocket Logarithms to Four Places. (Science Series No. 65.).....16mo, 0 50
leather, 1 00
Polleyn, F. Dressings and Finishings for Textile Fabrics.....8vo, *3 00
Pope, F. G. Organic Chemistry.....12mo, *2 25
Pope, F. L. Modern Practice of the Electric Telegraph.....8vo, 1 50
Popplewell, W. C. Prevention of Smoke.....8vo, *3 50
—— Strength of Materials.....8vo, *1 75
Porritt, B. D. The Chemistry of Rubber. (Chemical Monographs, No. 3.).....12mo, *0 75
Porter, J. R. Helicopter Flying Machine.....12mo, *1 25
Potts, H. E. Chemistry of the Rubber Industry. (Outlines of Industrial Chemistry).....8vo, *2 00
Practical Compounding of Oils, Tallow and Grease.....8vo, *3 50
Pratt, K. Boiler Draught.....12mo, *1 25
—— High Speed Steam Engines.....8vo, *2 00
Pray, T., Jr. Twenty Years with the Indicator.....8vo, 2 50
—— Steam Tables and Engine Constant.....8vo, 2 00
Prelini, C. Earth and Rock Excavation.....8vo, *3 00
—— Graphical Determination of Earth Slopes.....8vo, *2 00
—— Tunneling. New Edition.....8vo, *3 00
—— Dredging. A Practical Treatise.....8vo, *3 00
Prescott, A. B. Organic Analysis.....8vo, 5 00
Prescott, A. B., and Johnson, O. C. Qualitative Chemical Analysis...8vo, *3 50

Prescott, A. B., and Sullivan, E. C. First Book in Qualitative Chemistry. 12mo, *1 50

Prideaux, E. B. R. Problems in Physical Chemistry.....8vo, *2 00

Primrose, G. S. C. Zinc. (Metallurgy Series.).....(*In Press.*)

Pullen, W. W. F. Application of Graphic Methods to the Design of Structures.....12mo, *2 50

—— Injectors: Theory, Construction and Working.....12mo, *1 50

——Indicator Diagrams 8vo, *2 50

—— Engine Testing 8vo, *4 50

Pulsifer, W. H. Notes for a History of Lead.....8vo, 4 00

Putsch, A. Gas and Coal-dust Firing.....8vo, *3 00

Pynchon, T. R. Introduction to Chemical Physics.....8vo, 3 00

Rafter G. W. Mechanics of Ventilation. (Science Series No. 33.) 16mo, 0 50

—— Potable Water. (Science Series No. 103.).....16mo, 0 50

—— Treatment of Septic Sewage. (Science Series No. 118.)...16mo, 0 50

Rafter, G. W., and Baker, M. N. Sewage Disposal in the United States. 4to, *6 00

Raikes, H. P. Sewage Disposal Works.....8vo, *4 00

Randall, P. M. Quartz Operator's Handbook.....12mo, 2 00

Randau, P. Enamels and Enamelling.....8vo, *4 00

Rankine, W. J. M. Applied Mechanics.....8vo, 5 00

—— Civil Engineering.....8vo, 6 50

—— Machinery and Millwork.....8vo, 5 00

—— The Steam-engine and Other Prime Movers.....8vo, 5 00

Rankine, W. J. M., and Bamber, E. F. A Mechanical Text-book....8vo, 3 50

Raphael, F. C. Localization of Faults in Electric Light and Power Mains. 8vo, *3 00

Rasch, E. Electric Arc Phenomena. Trans. by K. Tornberg.....8vo, *2 00

Rathbone, R. L. B. Simple Jewellery.....8vo, *2 00

Rateau, A. Flow of Steam through Nozzles and Orifices. Trans. by H. B. Brydon.....8vo *1 50

Rausenberger, F. The Theory of the Recoil of Guns.....8vo, *4 50

Rautenstrauch, W. Notes on the Elements of Machine Design.8vo, boards, *1 50

Rautenstrauch, W., and Williams, J. T. Machine Drafting and Empirical Design.

Part I. Machine Drafting.....8vo, *1 25

Part II. Empirical Design.....(*In Preparation.*)

Raymond, E. B. Alternating Current Engineering.....12mo, *2 50

Rayner, H. Silk Throwing and Waste Silk Spinning.....8vo, *2 50

Recipes for the Color, Paint, Varnish, Oil, Soap and Drysaltery Trades.8vo, *3 50

Recipes for Flint Glass Making.....12mo, *4 50

Redfern, J. B., and Savin, J. Bells, Telephones (Installation Manuals Series.).....16mo, *0 50

Redgrove, H. S. Experimental Mensuration.....12mo, *1 25

Redwood, B. Petroleum. (Science Series No. 92.).....16mo, 0 50

Reed, S. Turbines Applied to Marine Propulsion..... *5 00

Reed's Engineers' Handbook.....8vo, *5 00

—— Key to the Nineteenth Edition of Reed's Engineers' Handbook..8vo, *3 00

—— Useful Hints to Sea-going Engineers.....12mo, 1 50

—— Guide to the Use of the Slide Valve.....12mo, *1 60

Reid, E. E. Introduction to Research in Organic Chemistry. (*In Press.*)
Reid, H. A. Concrete and Reinforced Concrete Construction.....8vo, *$5 00
Reinhardt, C. W. Lettering for Draftsmen, Engineers, and Students. oblong 4to, boards, 1 00
—— The Technic of Mechanical Drafting.....oblong 4to, boards, *1 00
Reiser, F. Hardening and Tempering of Steel. Trans. by A. Morris and H. Robson.....12mo, *2 50
Reiser, N. Faults in the Manufacture of Woolen Goods. Trans. by A. Morris and H. Robson.....8vo, *2 50
—— Spinning and Weaving Calculations.....8vo, *5 00
Renwick, W. G. Marble and Marble Working.....8vo, 5 00
Reuleaux, F. The Constructor. Trans. by H. H. Suplee.....4to, *4 00
Reuterdahl, A. Theory and Design of Reinforced Concrete Arches.8vo, *2 00
Reynolds, O., and Idell, F. E. Triple Expansion Engines. (Science Series No. 99.).....16mo, 0 50
Rhead, G. F. Simple Structural Woodwork.....12mo, *1 00
Rhodes, H. J. Art of Lithography.....8vo, 3 50
Rice, J. M., and Johnson, W. W. A New Method of Obtaining the Differential of Functions.....12mo, 0 50
Richards, W. A. Forging of Iron and Steel.....(*In Press.*)
Richards, W. A., and North, H. B. Manual of Cement Testing....12mo, *1 50
Richardson, J. The Modern Steam Engine.....8vo, *3 50
Richardson, S. S. Magnetism and Electricity.....12mo, *2 00
Rideal, S. Glue and Glue Testing.....8vo, *4 00
Rimmer, E. J. Boiler Explosions, Collapses and Mishaps.....8vo, *1 75
Rings, F. Concrete in Theory and Practice.....12mo, *2 50
—— Reinforced Concrete Bridges.....4to, *5 00
Ripper, W. Course of Instruction in Machine Drawing.....folio, *6 00
Roberts, F. C. Figure of the Earth. (Science Series No. 79.).....16mo, 0 50
Roberts, J., Jr. Laboratory Work in Electrical Engineering.....8vo, *2 00
Robertson, L. S. Water-tube Boilers.....8vo, 2 00
Robinson, J. B. Architectural Composition.....8vo, *2 50
Robinson, S. W. Practical Treatise on the Teeth of Wheels. (Science Series No. 24.).....16mo, 0 50
—— Railroad Economics. (Science Series No. 59.).....16mo, 0 50
—— Wrought Iron Bridge Members. (Science Series No. 60.).....16mo, 0 50
Robson, J. H. Machine Drawing and Sketching.....8vo, *1 50
Roebling, J. A. Long and Short Span Railway Bridges.....folio, 25 00
Rogers, A. A Laboratory Guide of Industrial Chemistry.....12mo, *1 50
Rogers, A. Industrial Chemistry.....8vo, *5 00
Rogers, F. Magnetism of Iron Vessels. (Science Series No. 30.).16mo, 0 50
Rohland, P. Colloidal and Crystalloidal State of Matter. Trans. by W. J. Britland and H. E. Potts.....12mo, *1 25
Rollins, W. Notes on X-Light.....8vo, *5 00
Rollinson, C. Alphabets.....Oblong, 12mo, *1 00
Rose, J. The Pattern-makers' Assistant.....8vo, 2 50
—— Key to Engines and Engine-running.....12mo, 2 50
Rose, T. K. The Precious Metals. (Westminster Series.).....8vo, *2 00
Rosenhain, W. Glass Manufacture. (Westminster Series.).....8vo, *2 00
—— Physical Metallurgy, An Introduction to. (Metallurgy Series.) 8vo, (*In Press.*)

Ross, W. A. Blowpipe in Chemistry and Metallurgy.....12mo, *2 00
Roth. Physical Chemistry.....8vo, *2 00
Rothery, G. C., and Edmonds, H. O. The Modern Laundry, 2 vols., 4to, half leather, *12 00
Rouillion, L. The Economics of Manual Training.....8vo, 2 00
Rowan, F. J. Practical Physics of the Modern Steam-boiler.....8vo, *3 00
—— and Idell, F. E. Boiler Incrustation and Corrosion. (Science Series No. 27.).....16mo, 0 50
Roxburgh, W. General Foundry Practice. (Westminster Series.).8vo, *2 00
Ruhmer, E. Wireless Telephony. Trans. by J. Erskine-Murray..8vo, *3 50
Russell, A. Theory of Electric Cables and Networks.....8vo, *3 00

Sabine, R. History and Progress of the Electric Telegraph.....12mo, 1 25
Sanford, P. G. Nitro-explosives.....8vo, *4 00
Saunders, C. H. Handbook of Practical Mechanics.....16mo, 1 00
leather, 1 25
Sayers, H. M. Brakes for Tram Cars.....8vo, *1 25
Scheele, C. W. Chemical Essays.....8vo, *2 00
Scheithauer, W. Shale Oils and Tars.....8vo, *3 50
Schellen, H. Magneto-electric and Dynamo-electric Machines....8vo, 5 00
Scherer, R. Casein. Trans. by C. Salter.....8vo, *3 00
Schidrowitz, P. Rubber, Its Production and Industrial Uses.....8vo, *5 00
Schindler, K. Iron and Steel Construction Works. 12mo, *1 25
Schmall, C. N. First Course in Analytic Geometry, Plane and Solid. 12mo, half leather, *1 75
Schmall, C. N., and Shack, S. M. Elements of Plane Geometry...12mo, *1 25
Schmeer, L. Flow of Water.....8vo, *3 00
Schumann, F. A Manual of Heating and Ventilation....12mo, leather, 1 50
Schwarz, E. H. L. Causal Geology.....8vo, *2 50
Schweizer, V. Distillation of Resins.....8vo, *3 50
Scott, W. W. Qualitative Analysis. A Laboratory Manual.....8vo, *1 50
Scribner, J. M. Engineers' and Mechanics' Companion..16mo, leather, 1 50
Scudder, H. Electrical Conductivity and Ionization Constants of Organic Compounds.....8vo, *3 00
Searle, A. B. Modern Brickmaking.....8vo, *5 00
—— Cement, Concrete and Bricks.....8vo, *3 00
Searle, G. M. "Sumners' Method." Condensed and Improved. (Science Series No. 124.).....16mo, 0 50
Seaton, A. E. Manual of Marine Engineering.....8vo 8 00
Seaton, A. E., and Rounthwaite, H. M. Pocket-book of Marine Engineering.....16mo, leather, 3 50
Seeligmann, T., Torrilhon, G. L., and Falconnet, H. India Rubber and Gutta Percha. Trans. by J. G. McIntosh.....8vo, *5 00
Seidell, A. Solubilities of Inorganic and Organic Substances.....8vo, *3 00
Seligman, R. Aluminum. (Metallurgy Series.).....(*In Press.*)
Sellew, W. H. Steel Rails.....4to, *12 50
—— Railway Maintenance .....(*In Press.*)
Senter, G. Outlines of Physical Chemistry.....12mo, *1 75
—— Text-book of Inorganic Chemistry.....12mo, *1 75

Sever, G. F. Electric Engineering Experiments.....8vo, boards, *1 00
Sever, G. F., and Townsend, F. Laboratory and Factory Tests in Electrical Engineering.....8vo, *2 50
Sewall, C. H. Wireless Telegraphy.....8vo, *2 00
—— Lessons in Telegraphy.....12mo, *1 00
Sewell, T. The Construction of Dynamos.....8vo, *3 00
Sexton, A. H. Fuel and Refractory Materials.....12mo, *2 50
—— Chemistry of the Materials of Engineering.....12mo, *2 50
—— Alloys (Non-Ferrous).....8vo, *3 00
—— The Metallurgy of Iron and Steel.....8vo, *6 50
Seymour, A. Modern Printing Inks.....8vo, *2 00
Shaw, Henry S. H. Mechanical Integrators. (Science Series No. 83.) 16mo, 0 50
Shaw, S. History of the Staffordshire Potteries.....8vo, 2 00
—— Chemistry of Compounds Used in Porcelain Manufacture....8vo, *5 00
Shaw, W. N. Forecasting Weather.....8vo, *3 50
Sheldon, S., and Hausmann, E. Direct Current Machines.....12mo, *2 50
—— Alternating Current Machines.....12mo, *2 50
Sheldon, S., and Hausmann, E. Electric Traction and Transmission Engineering.....12mo, *2 50
Shields, J. E. Notes on Engineering Construction.....12mo, 1 50
Shreve, S. H. Strength of Bridges and Roofs.....8vo, 3 50
Shunk, W. F. The Field Engineer.....12mo, morocco, 2 50
Simmons, W. H., and Appleton, H. A. Handbook of Soap Manufacture, 8vo, *3 00
Simmons, W. H., and Mitchell, C. A. Edible Fats and Oils.....8vo, *3 00
Simpson, G. The Naval Constructor.....12mo, morocco, *5 00
Simpson, W. Foundations.....8vo. (*In Press.*)
Sinclair, A. Development of the Locomotive Engine...8vo, half leather, 5 00
Sindall, R. W., and Bacon, W. N. The Testing of Wood Pulp.....8vo, *2 50
Sindall, R. W. Manufacture of Paper. (Westminster Series.)....8vo, *2 00
Sloane, T. O'C. Elementary Electrical Calculations.....12mo, *2 00
Smallwood, J. C. Mechanical Laboratory Methods. (Van Nostrand's Textbooks.).....12mo, leather, *2 50
Smith, C. A. M. Handbook of Testing, MATERIALS.....8vo, *2 50
Smith, C. A. M., and Warren, A. G. New Steam Tables.....8vo, *1 25
Smith, C. F. Practical Alternating Currents and Testing.....8vo, *2 50
—— Practical Testing of Dynamos and Motors.....8vo, *2 00
Smith, F. A. Railway Curves.....12mo, *1 00
—— Standard Turnounts on American Railroads.....12mo, *1 00
—— Maintenance of Way Standards.....12mo, *1 50
Smith, F. E. Handbook of General Instruction for Mechanics...12mo, 1 50
Smith, H. G. Minerals and the Microscope.....12mo, *1 25
Smith, J. C. Manufacture of Paint.....8vo, *3 50
Smith, R. H. Principles of Machine Work.....12mo, *3 00
—— Elements of Machine Work.....12mo, *2 00
Smith, W. Chemistry of Hat Manufacturing.....12mo, *3 00
Snell, A. T. Electric Motive Power.....8vo, *4 00
Snow, W. G. Pocketbook of Steam Heating and Ventilation. (*In Press.*)

Snow, W. G., and Nolan, T. Ventilation of Buildings. (Science Series No. 5.) 16mo, 0 50
Soddy, F. Radioactivity 8vo, *3 00
Solomon, M. Electric Lamps. (Westminster Series.) 8vo, *2 00
Somerscales, A. N. Mechanics for Marine Engineers 12mo, *1 50
—— Mechanical and Marine Engineering Science 8vo, *5 00
Sothern, J. W. The Marine Steam Turbine 8vo, *5 00
—— Verbal Notes and Sketches for Marine Engineers 8vo, *5 00
Sothern, J. W., and Sothern, R. M. Elementary Mathematics for Marine Engineers 12mo, *1 00
—— Simple Problems in Marine Engineering Design 12mo, *1 00
Southcombe, J. E. Chemistry of the Oil Industries. (Outlines of Industrial Chemistry.) 8vo, *3 00
Soxhlet, D. H. Dyeing and Staining Marble. Trans. by A. Morris and H. Robson 8vo, *2 50
Spang, H. W. A Practical Treatise on Lightning Protection 12mo, 1 00
Spangenburg, L. Fatigue of Metals. Translated by S. H. Shreve. (Science Series No. 23.) 16mo, 0 50
Specht, G. J., Hardy, A. S., McMaster, J. B., and Walling. Topographical Surveying. (Science Series No. 72.) 16mo, 0 50
Spencer, A. S. Design of Steel-Framed Sheds 8vo, *4 00
Speyers, C. L. Text-book of Physical Chemistry 8vo, *2 25
Spiegel, L. Chemical Constitution and Physiological Action. (Trans. by C. Luedeking and A. C. Boylston.) 1 25
Sprague, E. H. Hydraulics 12mo, 1 25
Stahl, A. W. Transmission of Power. (Science Series No. 28.) . 16mo,
Stahl, A. W., and Woods, A. T. Elementary Mechanism 12mo, *2 00
Staley, C., and Pierson, G. S. The Separate System of Sewerage.. 8vo, *3 00
Standage, H. C. Leatherworkers' Manual 8vo, *3 50
—— Sealing Waxes, Wafers, and Other Adhesives 8vo, *2 00
—— Agglutinants of all Kinds for all Purposes 12mo, *3 50
Stanley, H. Practical Applied Physics ..... (*In Press.*)
Stansbie, J. H. Iron and Steel. (Westminster Series.) 8vo, *2 00
Steadman, F. M. Unit Photography 12mo, *2 00
Stecher, G. E. Cork. Its Origin and Industrial Uses 12mo, 1 00
Steinman, D. B. Suspension Bridges and Cantilevers. (Science Series No. 127.) 0 50
—— Melan's Steel Arches and Suspension Bridges 8vo, *3 00
Stevens, H. P. Paper Mill Chemist 16mo, *2 50
Stevens, J. S. Theory of Measurements 12mo, *1 25
Stevenson, J. L. Blast-Furnace Calculations ..... 12mo, leather, *2 00
Stewart, G. Modern Steam Traps 12mo, *1 25
Stiles, A. Tables for Field Engineers 12mo, 1 00
Stodola, A. Steam Turbines. Trans. by L. C. Loewenstein 8vo, *5 00
Stone, H. The Timbers of Commerce 8vo, 3 50
Stopes, M. Ancient Plants 8vo, *2 00
—— The Study of Plant Life 8vo, *2 00
Stumpf, Prof. Una-Flow of Steam Engine 4to, *3 50
Sudborough, J. J., and James, T. C. Practical Organic Chemistry.. 12mo, *2 00
Suffling, E. R. Treatise on the Art of Glass Painting 8vo, *3 50
Sur, F. J. S. Oil Prospecting and Extracting 8vo, *1 00

Swan, K. Patents, Designs and Trade Marks. (Westminster Series.). 8vo, *2 00
Swinburne, J., Wordingham, C. H., and Martin, T. C. Electric Currents. (Science Series No. 109.) 16mo, 0 50
Swoope, C. W. Lessons in Practical Electricity 12mo, *2 00

Tailfer, L. Bleaching Linen and Cotton Yarn and Fabrics 8vo, *5 00
Tate, J. S. Surcharged and Different Forms of Retaining-walls. (Science Series No. 7.) 16mo, 0 50
Taylor, F. N. Small Water Supplies 12mo, *2 00
—— Masonry in Civil Engineering 8vo, *2 50
Taylor, T. U. Surveyor's Handbook ..... 12mo, leather, *2 00
—— Backbone of Perspective 12mo, *1 00
Taylor, W. P. Practical Cement Testing 8vo, *3 00
Templeton, W. Practical Mechanic's Workshop Companion. 12mo, morocco, 2 00
Tenney, E. H. Test Methods for Steam Power Plants. (Van Nostrand's Textbooks.) 12mo, *2 50
Terry, H. L. India Rubber and its Manufacture. (Westminster Series.) 8vo, *2 00
Thayer, H. R. Structural Design. 8vo.
Vol. I. Elements of Structural Design *2 00
Vol. II. Design of Simple Structures *4 00
Vol. III. Design of Advanced Structures ..... (*In Preparation.*)
—— Foundations and Masonry ..... (*In Preparation.*)
Thiess, J. B., and Joy, G. A. Toll Telephone Practice 8vo, *3 50
Thom, C., and Jones, W. H. Telegraphic Connections ..... oblong, 12mo, 1 50
Thomas, C. W. Paper-makers' Handbook ..... (*In Press.*)
Thompson, A. B. Oil Fields of Russia 4to, *7 50
Thompson, S. P. Dynamo Electric Machines. (Science Series No. 75.) 16mo, 0 50
Thompson, W. P. Handbook of Patent Law of All Countries 16mo, 1 50
Thomson, G. S. Milk and Cream Testing 12mo, *1 75
—— Modern Sanitary Engineering, House Drainage, etc 8vo, *3 00
Thornley, T. Cotton Combing Machines 8vo, *3 00
—— Cotton Waste 8vo, *3 00
—— Cotton Spinning. 8vo.
First Year *1 50
Second Year *2 50
Third Year *2 50
Thurso, J. W. Modern Turbine Practice 8vo, *4 00
Tidy, C. Meymott. Treatment of Sewage. (Science Series No. 94.) 16mo, 0 50
Tillmans, J. Water Purification and Sewage Disposal. Trans. by Hugh S. Taylor 8vo, *2 00
Tinney, W. H. Gold-mining Machinery 8vo, *3 00
Titherley, A. W. Laboratory Course of Organic Chemistry 8vo, *2 00
Toch, M. Chemistry and Technology of Mixed Paints 8vo, *3 00
—— Materials for Permanent Painting 12mo, *2 00
—— Chemistry and Technology of Mixed Paints ..... (*In Press.*)
Tod, J., and McGibbon, W. C. Marine Engineers' Board of Trade Examinations 8vo; *1 50

Todd, J., and Whall, W. B. Practical Seamanship.....8vo, *7 50
Tonge, J. Coal. (Westminster Series.).....8vo, *2 00
Townsend, F. Alternating Current Engineering.....8vo, boards, *0 75
Townsend, J. Ionization of Gases by Collision.....8vo, *1 25
Transactions of the American Institute of Chemical Engineers, 8vo.
Seven volumes now ready. Vol. I. to VII., 1908-1914....8vo, each, *6 00
Traverse Tables. (Science Series No. 115.).....16mo, 0 50
morocco, 1 00
Treiber, E. Foundry Machinery. Trans. by C. Salter.....12mo, 1 25
Trinks, W., and Housum, C. Shaft Governors. (Science Series No. 122.)
16mo, 0 50
Trowbridge, W. P. Turbine Wheels. (Science Series No. 44.)..16mo, 0 50
Tucker, J. H. A Manual of Sugar Analysis.....8vo, 3 50
Tunner, P. A. Treatise on Roll-turning. Trans. by J. B. Pearse.
8vo, text and folio atlas, 10 00
Turnbull, Jr., J., and Robinson, S. W. A Treatise on the Compound Steam-engine. (Science Series No. 8.).....16mo,
Turrill, S. M. Elementary Course in Perspective.....12mo, *1 25
Twyford, H. B. Purchasing.....8vo, *3 00
Tyrrell, H. G. Design and Construction of Mill Buildings.....8vo, *4 00
—— Concrete Bridges and Culverts.....16mo, leather, *3 00
—— Artistic Bridge Design.....8vo, *3 00

Underhill, C. R. Solenoids, Electromagnets and Electromagnetic Windings.....12mo, *2 00
Underwood, N., and Sullivan, T. V. Chemistry and Technology of Printing Inks.....8vo, *3 00
Urquhart, J. W. Electric Light Fitting.....12mo, 2 00
—— Electro-plating.....12mo, 2 00
—— Electrotyping.....12mo, 2 00
Usborne, P. O. G. Design of Simple Steel Bridges.....8vo, *4 00

Vacher, F. Food Inspector's Handbook.....12mo, *3 00
Van Nostrand's Chemical Annual. Third issue 1913....leather, 12mo, *2 50
—— Year Book of Mechanical Engineering Data.....(*In Press.*)
Van Wagenen, T. F. Manual of Hydraulic Mining.....16mo, 1 00
Vega, Baron Von. Logarithmic Tables.....8vo, cloth, 2 00
half morroco, 2 50
Vincent, C. Ammonia and its Compounds. Trans. by M. J. Salter.8vo, *2 00
Volk, C. Haulage and Winding Appliances.....8vo, *4 00
Von Georgievics, G. Chemical Technology of Textile Fibres. Trans. by C. Salter.....8vo, *4 50
—— Chemistry of Dyestuffs. Trans. by C. Salter.....8vo, *4 50
Vose, G. L. Graphic Method for Solving Certain Questions in Arithmetic and Algebra (Science Series No. 16.).....16mo, 0 50
Vosmaer, A. Ozone.....(*In Press.*)

Wabner, R. Ventilation in Mines. Trans. by C. Salter.....8vo, *4 50
Wade, E. J. Secondary Batteries.....8vo, *4 00

Wadmore, T. M. Elementary Chemical Theory.....12mo, *1 50
Wadsworth, C. Primary Battery Ignition.....12mo, *0 50
Wagner, E. Preserving Fruits, Vegetables, and Meat.....12mo, *2 50
Waldram, P. J. Principles of Structural Mechanics.....12mo, *3 00
Walker, F. Aerial Navigation.....8vo, 2 00
—— Dynamo Building. (Science Series No. 98.).....16mo, 0 50
Walker, F. Electric Lighting for Marine Engineers.....8vo, 2 00
Walker, J. Organic Chemistry for Students of Medicine.....8vo, *2 50
Walker, S. F. Steam Boilers, Engines and Turbines.....8vo, 3 00
—— Refrigeration, Heating and Ventilation on Shipboard.....12mo, *2 00
—— Electricity in Mining.....8vo, *3 50
Wallis-Tayler, A. J. Bearings and Lubrication.....8vo, *1 50
—— Aerial or Wire Ropeways.....8vo, *3 00
—— Motor Vehicles for Business Purposes.....8vo, 3 50
—— Refrigeration, Cold Storage and Ice-Making.....8vo, *4 50
—— Sugar Machinery.....12mo, *2 00
Walsh, J. J. Chemistry and Physics of Mining and Mine Ventilation, 12mo, *2 00
Wanklyn, J. A. Water Analysis.....12mo, 2 00
Wansbrough, W. D. The A B C of the Differential Calculus.....12mo, *1 50
—— Slide Valves.....12mo, *2 00
Waring, Jr., G. E. Sanitary Conditions. (Science Series No. 31.).16mo, 0 50
—— Sewerage and Land Drainage..... *6 00
Waring, Jr., G. E. Modern Methods of Sewage Disposal.....12mo, 2 00
—— How to Drain a House.....12mo, 1 25
Warnes, A. R. Coal Tar Distillation.....8vo, *2 50
Warren, F. D. Handbook on Reinforced Concrete.....12mo, *2 50
Watkins, A. Photography. (Westminster Series.).....8vo, *2 00
Watson, E. P. Small Engines and Boilers.....12mo, 1 25
Watt, A. Electro-plating and Electro-refining of Metals.....8vo, *4 50
—— Electro-metallurgy.....12mo, 1 00
—— The Art of Soap Making.....8vo, 3 00
—— Leather Manufacture.....8vo, *4 00
—— Paper-Making.....8vo, 3 00
Weather and Weather Instruments.....12mo, 1 00
paper, 0 50
Webb, H. L. Guide to the Testing of Insulated Wires and Cables.12mo, 1 00
Webber, W. H. Y. Town Gas. (Westminster Series.).....8vo, *2 00
Weisbach, J. A Manual of Theoretical Mechanics.....8vo, *6 00
sheep, *7 50
Weisbach, J., and Herrmann, G. Mechanics of Air Machinery....8vo, *3 75
Welch, W. Correct Lettering.....(*In Press.*)
Wells, M. B. Steel Bridge Designing.....8vo, *2 50
Weston, E. B. Loss of Head Due to Friction of Water in Pipes..12mo, *1 50
Weymouth, F. M. Drum Armatures and Commutators.....8vo, *3 00
Wheatley, O. Ornamental Cement Work.....8vo, *2 00
Wheeler, J. B. Art of War.....12mo, 1 75
—— Field Fortifications.....12mo, 1 75